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ELECTROLYTIC TREATMENT OF JOB SHOP METAL FINISHING WASTEWATER

Bruce E. Warner

New England Plating Company

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ELECTROLYTIC TREATMENT OF JOB SHOP METAL FINISHING WASTEWATER

Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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Full scale in-plant production studies demonstrated the reliability and economics of electrolytic cells containing beds of conductive particles between cathodes and anodes for reduction of hexavalent chromium and oxidation of cyanide in plating rinse water. The heavy metals are subsequently removed from the waste water by alkali precipitation. Seventy-five liter/min. (20 GPM) sized cells were employed for chromium and cyanide rinses. Chromium concentrations to 250 mg/liter and cyanide concentrations to 150 mg/liter were processed. Data were obtained with parallel equipment using chemical treatment for cost comparison. At low chromium concentrations (less than 25 mg/liter), chemical reduction was more economical. At higher concentrations (150 mg.liter), electrolytic reduction became the more economical process. In cyanide oxidation, the electrochemical process reduced direct costs associated with chlorination. Waste treatment costs, capital and operating, for the job shop are provided with an assessment of total costs on the price of services provided. Water conservation techniques are described. Experiences with tube settling equipment for removal of suspended solids and centrifuge for sludge concentration is provided.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Municipal Environmental Research Laboratory contributes to this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The studies for this report were undertaken to demonstrate the reliability and economics of a new electrolytic technique for treating metal finishing rinse waters in a full scale system under actual plant conditions. The electrochemical process employs a semi-conductive bed of carbon particles between the electrodes for the reduction of hexavalent chromium or the oxidation of cyanides commonly found in metal finishing wastes.

ABSTRACT

Full scale in-plant production studies demonstrated the reliability and economics of electrolytic cells containing beds of conductive particles between cathodes and anodes for reduction of hexavalent chromium and oxidation of cyanide in plating rinse water. The heavy metals are subsequently removed from the waste water by alkali precipitation.

Seventy-five liter/min (20 GPM) sized cells were employed for chromium and cyanide rinses. Chromium concentrations to 250 mg/liter and cyanide concentrations to 150 mg/liter were processed. Data were obtained with parallel equipment using chemical treatment for cost comparison.

At low chromium concentrations (less than 25 mg/liter), chemical reduction was more economical. At higher concentrations (150 mg/liter), electrolytic reduction became the more economical process. In cyanide oxidation, the electrochemical process reduced direct costs associated with chlorination.

Waste treatment costs, capital and operating, for the job shop are provided with an assessment of total costs on the price of services provided. Water conservation techniques are described. Experiences with tube settling equipment for removal of suspended solids and centrifuge for sludge concentration is provided.

This report was submitted in fulfillment of Project Number 12010 GUG by New England Plating Company, Inc., 31 Garden Street, Worcester, Massachusetts 01605, under the partial sponsorship of the Environmental Protection Agency.

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Other personnel who contributed in part to the project under the direction of Dr. Nicholas B. Franco are Mr. Robert Hess, Mr. William Litz and Mr. Robert Balouskus.

The cooperation of the management of Resource Control, Inc. and W. R. Grace & Co. is also to be recognized.

SECTION I

CONCLUSIONS

The use of the electrochemical process employing a semiconductive bed of carbon particles has been demonstrated in full-scale equipment under actual plant conditions for the reduction of hexavalent chromium and the oxidation of cyanides commonly found in metal finishing waste water.

While the process has successfully been demonstrated to be an effective and stable process for oxidation and reduction, the specific process equipment used in the demonstration is recognized to have some shortcomings.

The cells employed are larger than required for the low chromium concentration normally seen in the rinse waters after chromate conversion coatings on zinc and cadmium. This fact increased the operating and capital costs to the point where chemical reduction with acidic sodium bisulfite is economically more attractive. However, when concentrations of hexavalent chromium rise to the level normally experienced after chromium plating, the economics advantage shifts to the electrochemical approach.

In the reduction of hexavalent chromium, pH plays an important part. Lower pH values are required as the chromium concentration increases.

The same type and size cells used for cyanide destruction were smaller than required for the level of cyanide experienced in rinse waters during this demonstration. Higher voltages, together with increased cost of electricity, produced a cost reduction that was lower than anticipated. The operating cost advantage of this electrolytic process, in conjunction with the chemical destruction of cyanides, has been demonstrated. Final acceptance of the process by industry will undoubtedly depend upon improvement in cell design to improve yield and lower power costs.

There is adequate evidence that the electrochemical process does not produce cyanates and ammonia, which can result from chlorination. There is also a significant contribution to reduction in total dissolved solids when the electrolytic process is employed.

When used in the oxidation of cyanide, the process appears to be voltage-dominated, but in the ranges studied, no improvement in chromium reduction results from higher applied potentials.

During the demonstration of the electrochemical process, there was little, if any, destruction of the iron and nickel cyanide complexes. Parallel work shows that these complexes can be destroyed electrolytically. It is believed the presence of free cyanide along with these complexes inhibited the attack on the complexes themselves.

Considering the results obtained during the demonstration, and taking into account the state-of-the-art of hardware development, the electrochemical process offers economic incentives in operating costs when employed as a pretreatment prior to chemical oxidation or reduction to lower the amount of chemicals required for final treatment.

The demonstration project has provided information useful in reducing water consumption. The extended counterflow technique will provide a new approach for others to consider. The re-use of partially treated waste water has been demonstrated under rather selected applications as a further method to conserve water.

In solids handling, the tube settler approach to reducing capital and space requirements by 75 per cent has been demonstrated. A low-volume centrifuge, operating in a continuous-intermittent cycle, has been shown to be an aid in reducing the water content of sludges coming from waste treatment practices. Sludges having 0.5 per cent solids were concentrated to 30 percent solids.

SECTION II

RECOMMENDATIONS

In order to improve the economics of the electrochemical treatment, it is recommended that attention be directed towards cell configuration so that:

1. anode life can be extended,
2. with more acid resistant anodes, lower pH values may be used for greater chromium reduction efficiences, and
3. improvements can be made in bed cleaning techniques so as to promote bed fluidity and eliminate filtration requirements and labor attendant to these areas of operating expense.

In order to widen the application of electrochemical treatment, it is recommended that pilot studies be conducted in some of the more promising areas in the metal finishing industry:

1. oxidation of cyanide complexes common to metals normally considered lower in the electromotive series (copper, silver, gold),
2. extraction of metals from chelates commonly

used in cyanide free or low cyanide plating solutions,

3. extraction of metals from acid wastes (especially copper from etchants and pickling rinses), and
4. destruction of iron and nickel cyanide complexes found in strips and descalers.

In order to determine the extent of water conservation which can be achieved through the use of extended counterflow rinsing, in-plant studies to obtain production experience are required for plating solutions other than zinc and cadmium.

In order to further improve and more fully understand the advantages of tube settlers, it is recommended that:

1. various shapes of tubes be fully evaluated in a manner permitting comparison,
2. evaluations be conducted on various types of additives to enhance settling,
3. the role of recycling be fully evaluated,
4. attention be directed towards improvements in removal of solids from the settler after precipitation, and
5. studies be conducted on the role played by surface active chemicals and wetters in the settling rate of suspended solids.

In the use of centrifuges for sludge concentration, it is desirable to determine the optimum operating conditions when centrate recycling is employed.

SECTION III

INTRODUCTION

GENERAL

The Metal Finishing Industry is divided into two basic groups: captive shops and job shops.

The captive shops are found in manufacturing plants where, for one reason or another, it was deemed desirable to provide in-house finishing facilities for the various items being fabricated. The size of the captive shop will vary with the industry and with the specific plant itself.

Job shop metal finishing plants provide added-value services to manufacturers on a contract basis. The job shop size is as varied as the captive group.

Accurate statistics on the magnitude of the Metal Finishing Industry are virtually impossible to obtain. It is generally agreed that there are about 20,000 firms in the United States that can be included within this industry. Of this number, at least 3,500 are classified as job shops. It is believed that the annual dollar-added value for the industry exceeds $2 billion.

The geographic distribution is approximately 15 percent in southern and central New England, 22 percent in New York, New Jersey and eastern Pennsylvania, 35 percent in the midwestern states of Ohio, Indiana, Illinois, Michigan and Wisconsin, and 9 percent in California.

More detailed information on the scope of the industry can be found in the literature for those interested in the categorization and quantification of the industry.[1-5]

NEW ENGLAND PLATING COMPANY

New England Plating Company, 32 Garden Street, Worcester, Massachusetts, is considered a large metal finishing job shop by this industry's standards. It is within the top 10 percent of the number of firms when based upon the number of employees (74). Annual sales volume is considered average for this type of plant when one considers the number of employees and the types of operations performed.

The 3,340 square meter (36,000 square feet) plant is located on two floors. The greatest volume of work is done on five fully automatic processing machines. Four are for rack plating and one is for barrel plating. The finishes provided on these machines are: zinc, nickel and nickel-chrome. In addition, hand-operated hoist lines are used for barrel finishing of cadmium, copper and tin, as well as a hand-operated rack line for copper and tin. Most zinc plating receives chromate conversion coatings.

The base metal normally encountered in this finishing plant is steel. An insignificant amount of copper and copper alloys is occasionally processed. The results of this specialization are reflected in the cleaning cycles employed, the near absence of copper in the untreated waste water, and in the water re-use program developed.

The Metal Finishing Industry and its effect upon the environment has been well documented. New England Plating Company had been discharging untreated waste into a small stream adjacent to its plant. Other firms in the town used the sanitary sewerage system for discharge. New England Plating elected to provide complete treatment and continue to use the stream for discharge. The small stream was converted into an underground storm sewer by the city of Worcester and ultimately enters the Blackstone River. This same river receives the discharge from the sanitary sewage treatment plant. Prior to the installation of treatment facilities and adoption of water conservation practices, the discharge could be considered typical for the industry: too much water containing objectionable concentrations of materials considered harmful to the stream ecology.

New England Plating Company, as is true for many of the larger job shops, is continually changing its finishing requirements to reflect customer requirements and process improvements. During the course of this demonstration project, many process changes were made which varied the loading on the treatment facility. A few process changes were made to remain compatible with the treatment plant, but in large, the treatment system had to respond to the metal finishing changes.

OBJECTIVES

This demonstration project provides for the installation and operation of a waste treatment facility in a metal finishing job shop to:

(a) re-use untreated, partially treated and fully treated waste water to reduce the waste water volume by at least 50 percent;

(b) study and report on the effectiveness and economics of the semi-conductive bed electrolytic cell method of:

- reducing hexavalent chromium bearing rinse waters, and
- oxidizing cyanide bearing rinse waters, and

(c) study and report the effectiveness of the use of tube settling equipment for the removal of suspended solids, followed by sludge concentration in a centrifuge.

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SECTION IV

SOURCES OF WASTE WATER

GENERAL

At New England Plating Company, metal finishing operations generate three categories of waste water: continuously flowing rinses having relatively low concentrations of contaminants; periodic discharges of spent process solutions having relatively high contamination levels; and accidental discharges. The waste water may also be segregated and classified as cyanide bearing rinses and batch dumps, chromium bearing rinses and batch dumps, and those rinses and batch dumps that are free of cyanide and chromium.

Prior to waste treatment considerations, all waste water was intermixed and collected in trenches and drains leading to the adjacent stream. A typical analysis of the combined rinse water at a flow rate of 757 liters/minute (1/min) (200 GPM) is shown in Table 1. There would be minor variations from day to day depending upon the dragout of individual parts being processed. There would be significant changes in concentration for short periods when spent process solutions were discharged or in the case of an accidental discharge.

Table 1. TYPICAL ANALYSIS OF UNTREATED COMBINED WASTE

(milligrams/liter)

Cyanide, amenable	4
Hexavalent chromium	24
Trivalent chromium	11
Copper . . . . less than	0.5
Zinc . . . . less than	0.2
Nickel	4
Iron	2
Dissolved solids	1036
Suspended solids	46

The rinse water at individual process centers or plating steps was not analyzed and cannot be shown as a function of production volume. However, it is believed that others will be interested in the relationship of this typical analysis to the overall volume of production. This relationship of pollution to the amount of area being plated is shown in Table 2.

Table 2. POLLUTION AS A FUNCTION OF PRODUCTION

	mg/m^2	$lb/10^6 ft^2$
Cyanide	920	188
Hexavalent chromium	5,500	1,125
Trivalent chromium	2,520	516
Copper	112	23
Zinc	44	9
Nickel	900	188
Iron	460	94
Dissolved solids	238,000	48,600
Suspended solids	10,500	2,160

PROCESS DESCRIPTION

The process sequences vary slightly from one process center to the next depending upon the finishes being applied. However, the basic steps of surface preparation through cleaning and pickling of base metal, plating and post treatment of plated surfaces remain constant.

The sequence of steps in preparing the surfaces for plating is shown in Figure 1. On most cycles, counterflow rinsing is employed after these cleaners or pickles.

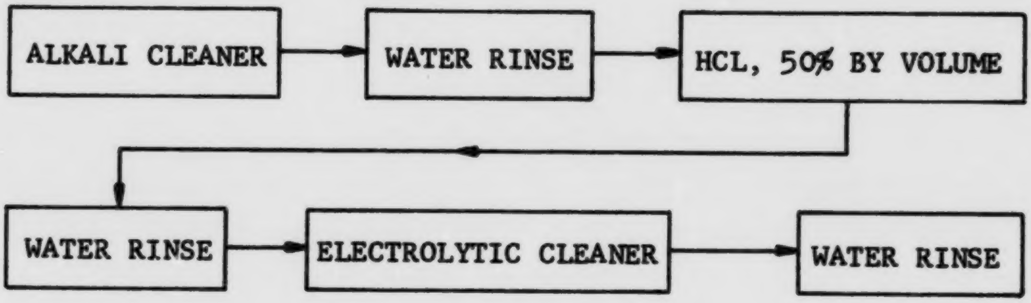

Figure 1. Surface preparation process

Prior to nickel plating, a dilute acid dip and water rinse follow the electrocleaner to provide a slightly acidic film on the surface as the parts enter the nickel plating tank.

Following the surface preparation steps, various plating solutions are used to meet the needs of customers. Zinc and cadmium plating are done in conventional cyanide plating solutions having bath compositions most favorable to rack or barrel plating. Nickel plating is accomplished in proprietary bright nickel solutions common to the industry. The chromium plating solution is a 240 g/l (32 oz/gal.) bath using proprietary self-regulating and foam blanket producing additives. Copper plating from conventional cyanide solutions is normally provided only as a strike prior to nickel or tin plating. Tin is plated from an alkaline stannate solution. Typical plating solution composition can be found in the references.[8]

Rinsing following plating is as varied as one would expect in a widely diversified job shop. In general, the types of rinses used are similar to those described by Olson.[7] Dragout recovery tanks are employed after nickel and chromium plating. Counterflow rinses are used extensively following all plating steps. A more detailed discussion on rinsing is provided later in the report in Section V, Water Conservation.

The sequence of operations following zinc plating is shown in Figure 2. Again space requirements on individual machines regulate the use of rinsing techniques.

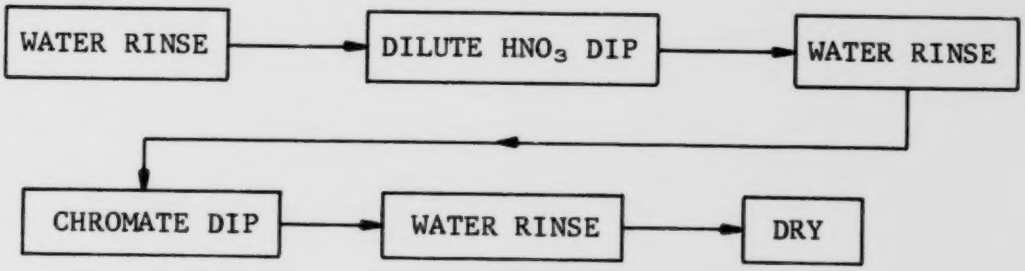

Figure 2. Post-treatment of zinc plate

Where practical, analytical control provides for long solution life, and plating solutions themselves are seldom if ever dumped. Other process solutions when spent are discharged on a periodic basis which varies from once in several months to once per day. On a monthly basis, the following volumes are dumped:

cyanide bearing solutions - 3,800 l (1,000 gal.)
chromium bearing solutions - 38,000 l (10,000 gal.)
non-CN/CR bearing solutions - 34,000 l (9,000 gal.)

OTHER WASTE WATER SOURCES

In addition to the main sources of rinses and batch dumps, there were other sources of waste water that contributed to the pollution loading. Steam condensate, while originally a problem, was collected and returned to the boiler for re-use. Open-ended cooling water, used to maintain temperature in zinc plating, was replaced with a recirculating coolant system chilled by refrigeration. Most of these other pollution problems were resolved prior to the flow measurements used to define the raw waste water magnitude given earlier in this report.

Prior to waste treatment and water conservation concern, rinse waters contributed approximately 60 kg (130 lb) of cyanide and 90 kg (200 lb) of hexavalent chromium per month. The batch discharge of spent solutions introduced an additional 200 kg (440 lb) of cyanide and 35 kg (77 lb) of hexavalent chromium.

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SECTION V

WATER CONSERVATION

GENERAL

Most waste treatment systems are significantly affected by the volume of waste water produced by rinsing operations in the various metal finishing processes. As the volume decreases, with a corresponding increase in contamination level, invariably the capital cost is reduced. When water was considered a readily available and low cost material, the Metal Finishing Industry used excessive quantities. Over the years, as increasing attention was focused on industrial waste treatment, more and more attention has been paid to rinsing itself. Previously the only criterion for rinsing had been the one of maintaining quality. The results of considerable effort by many concerned with rinse water volume reduction have been published during the last fifteen years.

Tallmadge, et al[8-13] and Kushner[14] have provided both the metal finisher and the waste treatment designer with formulation for determining contaminant level at various flow rates. These theoretical relationships are based upon the assumption that there is instantaneous and complete mixing. As a result, the calculated values are seldom realized in either experiments or in production unless mechanical aids to rinsing are employed. Kramer[15] reports good correlation between theoretical rinsing and production rinsing for rack plating, and poor comparison for barrel plating. The concept of theoretical rinsing to predict contaminant levels and flow rates has never been fully accepted. This is because the plater recognizes that the predicted values represent ideal conditions and therefore are only a fraction of the observed values.

Many excellent articles on the mechanical aspects of rinsing have been published. Pinkerton[16], Gary[17], Lancy and Ceresa[18-20] as well as Spring[21] and Tween[22] offer advice on techniques to improve rinsing and to reduce water consumption. Drip stations, dragout recovery tanks, counterflow rinses and spray rinses are important techniques to reduce both the volume of rinse water and the contamination level. In some facilities, air blow-off, fog or mist sprays, and drainboards offer additional methods of reducing the problems attendant to waste treatment. Circulation within the rinse tank caused by bottom entry of incoming water and air agitation as well as agitation of the work pieces being rinsed assist in obtaining the desired results predicted by the theoretical rinsing formulae.

Delos[23] and many others recommend the use of physical means to restrict the flow of water in any given set of circumstances. Both simple and sophisticated devices are readily available to remove from the operators' control the means of changing the water flow rate.

The plater has been slow to accept reduction in water consumption. He realizes the advantages of many of the physical or mechanical aids to rinsing, but has been reluctant to trust any significant reduction in water flow. His main concern has been that he has no guidelines as to how contaminated the rinse water may become before the quality of his finishing operations suffer. Barnes[24] has reported statistics on the range of contamination level and frequency of variation of concentration. He also reports tolerances for contaminants in rinsing to produce clean work at this installation. However, how these maximum contamination levels were established is not given. Graham and Pinkerton[25] use 1000:1 dilution as being borderline rinsing and 5000:1 dilution as being good rinsing. It must be realized that these figures are suitable for some operations but not all. The industry can only use the term "adequate rinsing" without defining it in other than general terms. These same authors point out the importance of reducing volumes only by the application of plating know-how.

Until the Metal Finishing Industry determines how dirty rinse water may become before process solution and product quality degradation are unacceptable, the plater will continue to use excess water and approach water use reduction with extreme reluctance and caution. It is the intent of this study to provide additional operating data so that further confidence will be gained that significant volume reductions are possible.

WATER CONSERVATION AT NEW ENGLAND PLATING COMPANY

Prior to considerations for waste treatment, excessive water was used for rinsing operations. The main concern was to maintain an adequate flow to prevent the contamination of process solutions and to maintain a high quality of work being processed. Although water costs were low, effort had been put forth to minimize water costs. Consequently, while positive steps towards reducing water use were underway, the quantity used was still well in excess of that required as a minimum.

During the past three years as plans were put into effect for treatment of waste water, additional modifications of existing metal finishing equipment were made to reduce water consumption. As new equipment was installed, many of the mechanical and physical aids to rinsing and water volume reduction mentioned earlier were incorporated. Most of the techniques mentioned earlier in this report were employed.

The studies conducted under this demonstration grant deal mainly with the re-use of rinse water. The results of the water conservation program at New England Plating are being reported under:

- Re-use of Untreated Water
- Re-use of Partially Treated Water
- Re-use of Fully Treated Water
- Other Techniques

Re-use of Untreated Rinse Water

Fresh water when introduced into a rinse tank becomes contaminated with the process chemicals on the work pieces. In many cases, this contamination level is low enough to permit re-use of the water for less demanding rinsing. One well versed with metal finishing technology has little trouble finding other uses for these untreated waste waters.

Counterflow Rinsing -

The most widely employed technique for re-use of untreated rinse water is known as counterflow rinsing. In this application, the water is used in two or more adjacent rinse stations with the flow of water being counter to the flow of the work pieces. Olson[26] provides an excellent discussion of this technique. This technique is used extensively at New England Plating Company where:

- the concentration of the process solution is high,
- extremely good rinsing is essential for quality,
- the solution being removed is difficult to rinse, and
- space permits.

Extended Counterflow Rinsing -

The counterflow rinse system described in the preceding paragraph is well documented in the literature. In most uses, it is limited to a single process solution. A logical extension of the counterflow technique is to re-use the water still another time. This "Extended Counterflow" can be applied successfully in cleaning cycles and with many plating processes themselves. With this technique, the water used for rinsing following a given process solution is the source of water for rinsing prior to that given process solution. For example, the rinse water following zinc plating is used as the rinse water prior to zinc plating and after the preceding cleaning step.

Figure 3 shows in a schematic diagram how this extended counterflow rinsing was accomplished in cleaning operations on automatic plating machines at New England Plating. On one zinc plating machine, the flow was reduced from 39 l/min (10.3 GPM) to 10.6 l/min (2.8 GPM) after the plumbing change. On other machines, flow reductions were 30 l/min (7.9 GPM) to 9.8 l/min (2.6 GPM) and 30 l/min (7.9 GPM) to 6.4 l/min (1.7 GPM).

These results provided the basis for similar plumbing changes throughout the facility. Since the rinse water leaving the pickling rinse station is acidic, it should be obvious that the work pieces are experiencing "chemical rinsing" in the cleaner rinse tank. The data shows that enough acid is

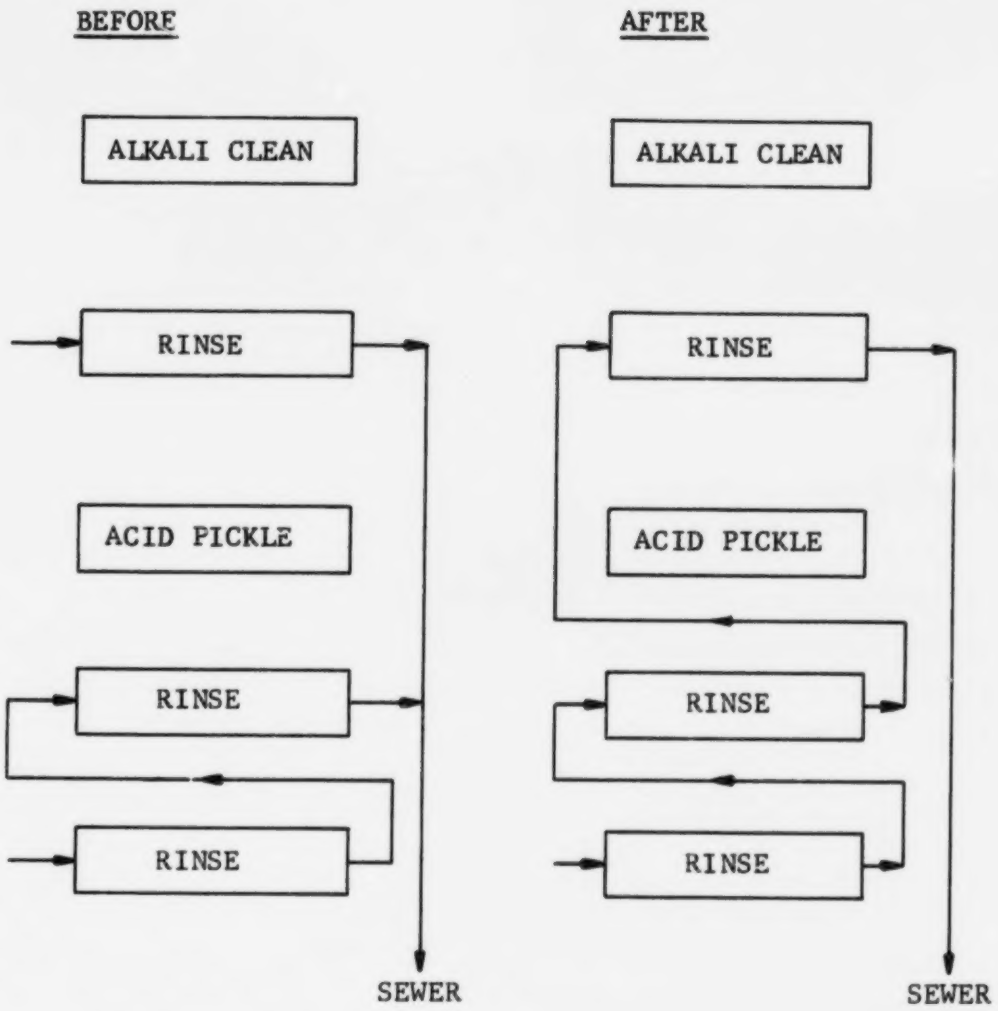
BEFORE
AFTER
ALKALI CLEAN
ALKALI CLEAN
RINSE
RINSE
ACID PICKLE
ACID PICKLE
RINSE
RINSE
RINSE
RINSE
SEWER
SEWER

Figure 3. Extended counterflow rinsing - cleaning

carried into the cleaner rinse tank to neutralize all cleaner dragout. In this manner no alkali is being carried over on the work pieces when they are immersed in the pickle, and longer pickle life is realized.

Figure 4 illustrates how this extended counterflow rinsing was accomplished in the plating process itself to reduce the hydraulic loading on the waste treatment facility. At New England Plating, this approach was used with zinc plating. The flow rate is adjusted to provide adequate rinsing following the plating process. The same water is then used prior to plating. Fresh water previously used in this rinse tank was discontinued. A typical flow rate of 6.5 l/min (1.7 GPM) produces cyanide concentrations in the range of 125-300 mg/l in the final overflow to the sewer.

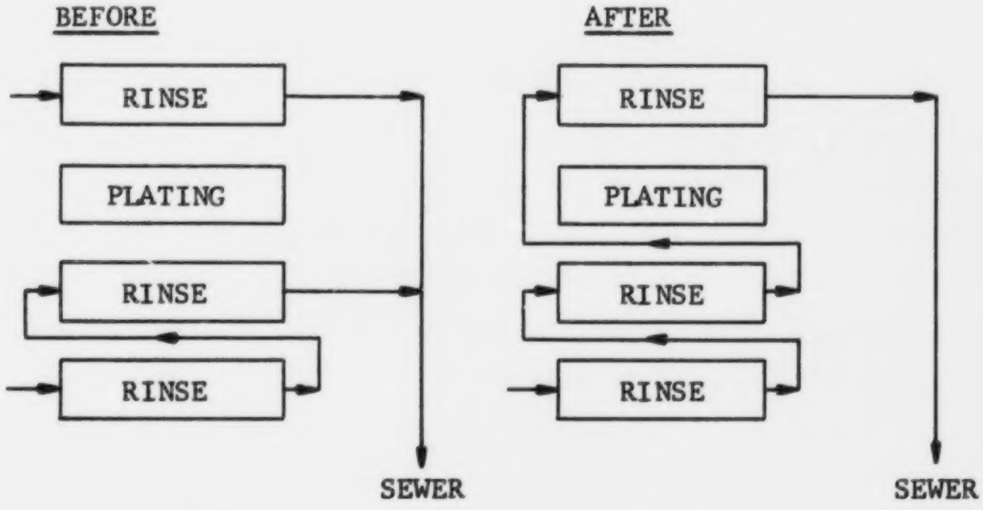

Figure 4. Extended counterflow rinsing - plating

Analysis of the data shows that the work pieces prior to plating are being rinsed with dilute plating solution. A slight amount of plating solution is being returned to the plating tank as the work pieces carry in this rinse water. More significant is the fact that the conventionally employed cyanide soak prior to plating is eliminated together with its periodic neutralization.

Figure 5 shows how the extended counterflow rinsing technique can be applied to hot water rinses. Prior to the concern for waste treatment, this plant had stagnant final hot water rinses in virtually every process line to aid in drying of work pieces, as is common in the industry. To minimize water stains on the plated parts, these stagnant rinses were dumped at least once a day. At the time of dumping, the water was still low in contamination level and in many ways suitable for less demanding rinses. At New England Plating, it was decided to convert these stagnant rinses to flowing rinses, with the discharge directed to the previous rinse station. Complete volume replacement would occur during the normal life of the hot water rinse between dumps. That is, a 1800 l (480 gal.) stagnant hot water rinse tank, which had normally been discharged every eight hours, was converted to a continuous flow rinse station with water flowing at a rate of 3.8 l/min (1 GPM) so that total volume replacement would take place in the same eight-hour period.

It was realized that while the rinse tank would never be as clean as in previous practices, it would also never be as

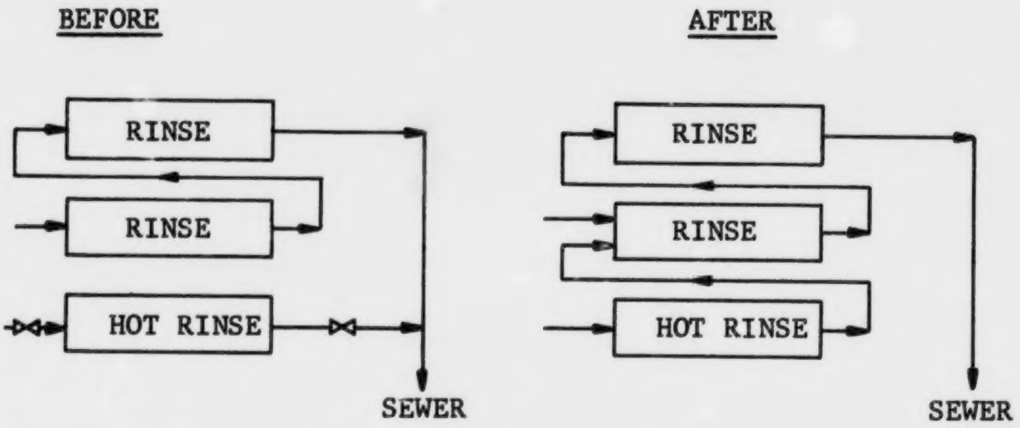

Figure 5. Extended counterflow rinsing - hot water rinse

contaminated. To keep this from becoming an additional hydraulic burden on the waste treatment facility, a corresponding reduction of fresh water was made in the rinse station prior to the hot water rinse. No change in the volume of flowing rinse water was realized by this re-use of untreated rinse water. The treatment facility actually received its benefits from the plumbing change, as there were no longer any surges of hot contaminated rinse water to drain or treat. Plating quality was slightly better, since the incidence of hard water stains was reduced. The additional steam required to heat the small amount of water flowing into the final hot water rinse tank is considered negligible when compared to the demand for heating a complete tank of fresh cold water on a daily basis.

Re-use of Partially Treated Water

Partially treated water is considered that water that has been rendered innocuous as far as dissolved salts are concerned, yet does not have the suspended solids removed. At New England Plating Company, partially treated water consists of a combination of: (1) rinses following alkaline cleaners and acid pickles with pH adjusted to near neutral; and (2) the discharge from the cyanide treatment system with its pH also adjusted to the same range. There are many uses for this second class water in a diversified plating shop, for example, maintenance cleaning or after stripping of rejects. On the other hand, one would rule out its application in such critical points as final hot water rinses (because of the high solids content) or for process solution make-up water.

Partially treated rinse water has proven an effective substitute for fresh water at New England Plating. In referring to Figure 1, Surface Preparation Process, it will be noted that rinse water is required following the hydrochloric acid pickle. Under normal production conditions, this rinse tank is at a pH of about 2. Neutral water supplied to this tank would accomplish the desired result of rinsing the acid from the work pieces. If the source of the rinse water is relatively high in suspended solids (as in the case of the second class water), one would expect the metal hydroxides to redissolve. At New England Plating the make-up water for most rinses after acid pickling has been converted to partially treated waste water without any adverse effect on plating quality or process solution life.

The re-use of partially treated waste water does not reduce the expense of the pretreatment that is required to establish an adequate quality of secondary water. The advantage is derived from the reduction in hydraulic capacity of equipment to remove suspended solids. At New England Plating, the re-use of partially treated waste water will result in a reduction of 33 percent in the size of solids separation equipment, as the amount of partially treated waste water that does not have to pass through the settler will be reduced by that amount. The total amount of solids removed remains the same.

Re-Use of Fully Treated Rinse Water

Fully treated water is considered to be water that has been rendered innocuous as far as dissolved salts are concerned and has had the suspended solids removed to practical limits. At the time this report is being prepared, the complete solids handling facility has not been used extensively. Data obtained under the Solids Handling Section of this report indicate good solids removal from the tube settler. However, based upon the success of the re-use of partially treated waste water, one can only speculate at this point as to the advisability of replacing the secondary water source with a tertiary source (namely, water treated for solids removal).

The primary concern involving the re-use of fully treated rinse water is one of accidental contamination with ions that are not compatible with the projected use. At New England Plating, waste water that passes through the solids removal equipment includes waste water from the chromium treatment process. It should be noted that the chromium bearing stream is excluded from the partially treated waste water. While the waste treatment engineer might not be aware of the following, the plater knows from experience that trace contamination with hexavalent chromium can cause severe plating problems. For this reason alone the re-use of fully treated rinse water may never reach full fruition. It is concluded, therefore, that there are no advantages to using fully treated waste water over partially treated waste water.

Other Techniques

While most of the attention during this program was directed towards the re-use of water for conservation purposes, a complete picture should include a discussion of other pertinent techniques directed towards reducing the amount of water.

Dragout Recovery -

Dragout recovery tanks are used following several plating solutions. Only those plating baths that are heated can use this approach to reducing the amount of solution that is carried into the flowing rinses. The stagnant rinse following the plating solution is used as make-up to replace the water lost from the bath by evaporation. Fresh water is added only to the dragout recovery tank to maintain its level.

To insure that the recovered solution will be used for make-up, provisions must be made so that it can be readily returned to the process tank in an easy or uncomplicated manner. The operator must prefer to use the recovery system instead of fresh water. Manual transfer is perhaps the poorest way to provide for the return of solution. A bucket for transfer will not be used in place of opening a water valve to add water. Automatic provisions for solution transfer are the only way to maximize dragout recovery systems.

Draining -

Where automatic transfer of work pieces is being accomplished, a definite pause in the cycle after the racks are withdrawn from the plating solutions will show a reduction in contamination level in rinses and permit less water to be used. In a similar manner, a slowing of the transfer mechanism during the withdrawal cycle is effective. Blow-off of solution as the racks pass through an air knife above the process tank can return as much as 50 percent of the solution. When manual processing of work pieces is being done, it is more difficult to obtain the same advantages of draining -- even though thorough employee indoctrination is used.

Control of Flow -

It is believed that sufficient flow controls have been established at New England Plating Co., yet enough flexibility has been built into the system to adjust for the variability required by the quality of parts being plated. All attempts were made to provide "convenient" controls at each process center to obtain the maximum cooperation from the operators.

Each process center is provided with its own water distribution system, including a main shut-off valve and individual flow control valves installed at each rinse tank. The main control valve minimizes the need for operator adjustment of flow control valves at start-up. One place to turn water on or off simplified start-up and shut-down procedures. Now the readjustment of flow control valves is only to accommodate the needs of work in process.

When one or more process centers is brought on line or is shut down, there can be a significant change in water pressure in the main supply pipes distributing water to each process center. An increase in pressure to a given process center will result in an increase in water flow. In a like manner, a reduction in water pressure will result in a reduction in water flow. Prior to the concern for water conservation, flow control valves were set to accommodate the lowest water pressure. When other process centers were shut down, the pressure would increase and more than required water would flow. It was desirable to eliminate this variable. Pressure reducing valves were installed in each water line supplying each center. The discharge pressure was set for the condition when all process centers were in use (at the lowest pressure in the main supply line). In this manner, at no time was the pressure supplied to any given center greater than that used to set the flow control valves, even though the main supply line pressure increases.

Other techniques to restrict the flow at a given process center were evaluated. While many provided good results, none were more economical than the use of pressure-reducing valves.

In one station, a wide range of flow is necessitated by the process itself. The hand-operated barrel line consumes a large volume of water for a short period of time when the barrel is immersed in the rinse tank, and little or no flow is required when the barrel is elsewhere in the cycle. Attempts to average the flow in the rinse tank reduced rinsing effectiveness and quality and/or production suffered. A solution was provided by the installation of automatic reset timers and solenoid valves. When the barrel is immersed in the rinse tank, the operator presses the timer button, the valve opens and water is admitted to the rinse tank. After the barrel is removed from the tank, the timer automatically stops the water flow until the cycle is repeated. In this manner, the turning off of a large volume of water was removed from the operator's control, yet adequate rinsing is available when needed.

Air Agitation -

As means to restrict the flow of water were installed, it became increasingly important that the maximum use of existing rinse water had to be made. Rinsing, per se, is the dilution of the film on the surface of the work pieces to a lower concentration. Physical means to accelerate this dilution (or mixing) will result in better rinsing and/or less water consumption. In hand-operated lines, agitation of the plating racks accelerates the film dilution. In automatic machines, work piece agitation becomes expensive. When the volume of rinse water was of less concern, excessive water flows increased the rate of film dilution, as the agitation caused by the water flow aided in film dilution and approached the theoretical rinsing discussed earlier.

Since excessive water flow was undesirable from a water treatment standpoint, other attempts to displace the film of solution on the work pieces were employed. The most effective technique was the use of air agitation in the rinse tanks. Headers were designed and installed in the bottom of all rinse tanks, so that the bubbles of air would increase solution agitation as they rose to the surface of the tank.

Air agitation permitted the use of a minimum amount of water for rinsing. In addition, it created the impression among the operators that they were obtaining the same degree of rinsing that was apparent before air agitation when large water flows were standard operating procedure.

Proof of Rinsing Adequacy -

Prior to evaluations, water flows were set at "best estimate" by operators. Based upon the successes in more important rinse areas (final rinsing, cleaning, etc.) contaminant measurement following other process solutions were done to see what other water economies could be realized. Many cases showed that good rinsing was possible with lower flows.

Following the "neutralizer dip" used after zinc or cadmium plating and prior to chromate coating, water flows were cut by 50 percent. The pH of the rinse water on the zinc plater went from 7.0 to 6.0. The flow following the same dip on another plater was then set to average at a pH of 6.0.

With adequate documentation of contamination levels in other rinse stations, confidence was established that less water could be used.

Chemical Rinsing -

The use of neutralizing chemicals as an aid in rinsing is common in the Metal Finishing Industry. Following cyanide copper plating, for example, most platers use a dilute sulfuric acid dip prior to nickel plating. This dip insures the absence of any alkaline film on the surfaces of the work in process and protects the pH of the nickel plating bath from undue alkali being dragged into the tank. In a similar manner, many employ dilute nitric acid dips after zinc plating and prior to chromate conversion coatings.

At New England Plating, an example exists wherein the addition of a chemical rinse had a significant effect on waste water volume reduction. The unit processes on a cadmium plating automatic were compared before and after the water conservation program began. Before recent concern for water use reduction, 48 l/min (12.5 GPM) of rinse water was required to obtain adequate rinsing prior to chromate coating. A counterflow rinse following plating, together with the addition of an acid dip and its rinses reduced the flow to 11.5 l/min (3.0 GPM). This machine was converted at a later time to zinc plating.

Personnel Factors

The best of intentions in water conservation efforts are meaningless unless those operators responsible for production and quality are well aware of the ultimate desires of management. Educational sessions directed towards keeping the operators informed of the need for water conservation and individual briefing for each process center as changes were initiated improved the picture. If the operator is not aware of the objectives for his individual area, he will develop methods to overcome water conservation techniques that he feels are forced upon him. The need for maintaining operator awareness is necessary on a continuing basis.

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SECTION VI

WASTE TREATMENT FACILITY

GENERAL

The waste treatment facility installed at New England Plating Company provides for segregation of waste by both type and concentration. The various subsystems are based upon the electrolytic reduction of hexavalent chromium and oxidation of cyanide, the precipitation of heavy metal hydroxides by pH adjustment and the removal of suspended solids with concentration of sludges. In addition to the electrolytic treatment processes, chemical means for oxidation/reduction reactions have been installed to obtain operating cost data for comparison purposes and to provide back-up treatment processes for the electrolytic treatment processes.

WASTE ISOLATION TECHNIQUES

Three separate drain systems were installed for flowing rinse waters. These drains segregate the wastes into those that are chromium bearing rinses, cyanide bearing rinses and rinses free of cyanides and chromium compounds. Spent process solutions that are dumped periodically are segregated into those which are cyanide bearing, chromium and acid bearing and non-cyanide alkali bearing. These waste streams drain by gravity to sumps located in the lowest section of the plant from where the waste water is pumped to appropriate subsystems. Accidental discharges, process equipment wash water and any other floor spills find their way into an old floor trench system and are collected with non-cyanide alkali batch dumps. All drains are piped to the appropriate sump to preclude accidental contamination that is possible when using trenches for sewers. Each sump is equipped with a high level alarm to alert operators when more water is entering than can be removed by the sump pumps. This safety feature was incorporated to prevent sumps from overflowing unnoticed, thus permitting isolated wastes to intermix and overtax the floor spill collection system.

DESIGN BASIS

The chromium rinse water treatment process was designed for a hydraulic loading of 150 l/min (40 GPM). Considering the concentrating effect to be experienced when chromium waste water was isolated, it was expected that these combined rinses would contain hexavalent chromium in the order of magnitude of 120 mg/l. Electrochemical treatment cells were selected that were believed to treat concentrations as high as 200 mg/l.

The cyanide rinse water treatment process was designed for a hydraulic loading of 115 l/min (30 GPM). Considering the concentration effect produced by isolation, it was expected that the cyanide bearing rinse waters would contain cyanide in the order of magnitude of 30 mg/l. Electrochemical treatment cells were selected that were believed to treat concentrations as high as 100 mg/l (although experience was slight in this potential application.)

The volume of those rinses known to be free of cyanide and chromium compounds and whose treatment requires pH adjustment was estimated to be 225 l/min (60 GPM). Since the pH adjustment system would also service treated cyanide rinse water to lower its pH, the pH system was sized for a hydraulic loading of 380 l/min (100 GPM). Normally this combined waste would be slightly acidic. When no treated cyanide rinse water was entering the system, the pH would be quite acidic. Conversely, when only treated cyanide rinse water entered the system, the waste would be alkaline.

The batch treatment processes were designed to handle chromium bearing waste at 11,400 l (3000 gal.) per week, cyanide bearing waste at 850 l (225 gal.) per week and non-CN/Cr bearing waste at 22,800 l (6000 gal.) per week.

The equipment for removing suspended solids from flowing rinse water was initially sized for a hydraulic loading of 570 l/min (150 GPM) at a normal suspended solids content of 100-200 mg/l. In order to maintain this relatively low solids concentration, the design took into consideration that solids generated by batch neutralization processes would not pass through the suspended solids removal equipment. The concentration of solids in the sludge from settling of suspended solids was expected to be in the range of 0.5-1 percent. Suspended solids coming from batch neutralization were expected to be in the range of 0.5 percent to 6 percent (with occasions where 15 percent would be reached).

Contingency factors that were also a part of the design basis considered the newness of the electrochemical treatment process and the lack of significant production experience. The chromium treatment process included the capability of converting to acidic-bisulfite reduction of hexavalent chromium. The electrochemical treatment process for cyanide oxidation was followed by a chemical oxidation system using sodium hypochlorite.

The combined effluent from the treatment facility considered significant re-use of treated rinse water to reduce the hydraulic flow to less than 380 l/min (100 GPM). It was anticipated that the discharge to the stream would have the characteristics as shown in Table 3 and be in the pH range of 6.5 - 8.5.

Table 3. ANTICIPATED EFFLUENT

(milligrams/liter)

Cyanide, amenable	0.1
Chromium, hexavalent	0.2
Chromium, trivalent	0.1
Copper	0.5
Zinc	1.2
Iron	0.1

The concentrations pertain to dissolved contaminants. It was realized that some portion of the 20 mg/1 of suspended solids anticipated would contain metallic hydroxides.

RINSE WATER TREATMENT

Details of the subsystems installed at New England Plating follow. Schematic flow diagrams are provided as an aid to the explanation. Operating conditions are stated. The results of the various studies conducted are to be found in Section VII, Demonstration of Treatment.

Chromium Rinse Water Treatment

Figure 6 should be referenced to assist in the description of the treatment system for chromium bearing rinse waters. The combined chromium bearing rinse waters that have been isolated from other process water drain by gravity into a collection sump. The sump is equipped with a level control, a high level alarm and a pump for transporting the water into the chromium rinse surge tank.

The chromium bearing rinse waters entering the surge tank have a pH range of 2 - 6.5. The electrolytic treatment process for reduction of chromium from the hexavalent to the trivalent state is most efficient at low pH. Therefore, these raw rinse waters flow through a pH control chamber upon entering the surge tank. This chamber is equipped with an air agitation header and a pH probe and has as auxiliary equipment a pH controller which actuates a proportional control feed pump delivering dilute sulfuric acid from a storage

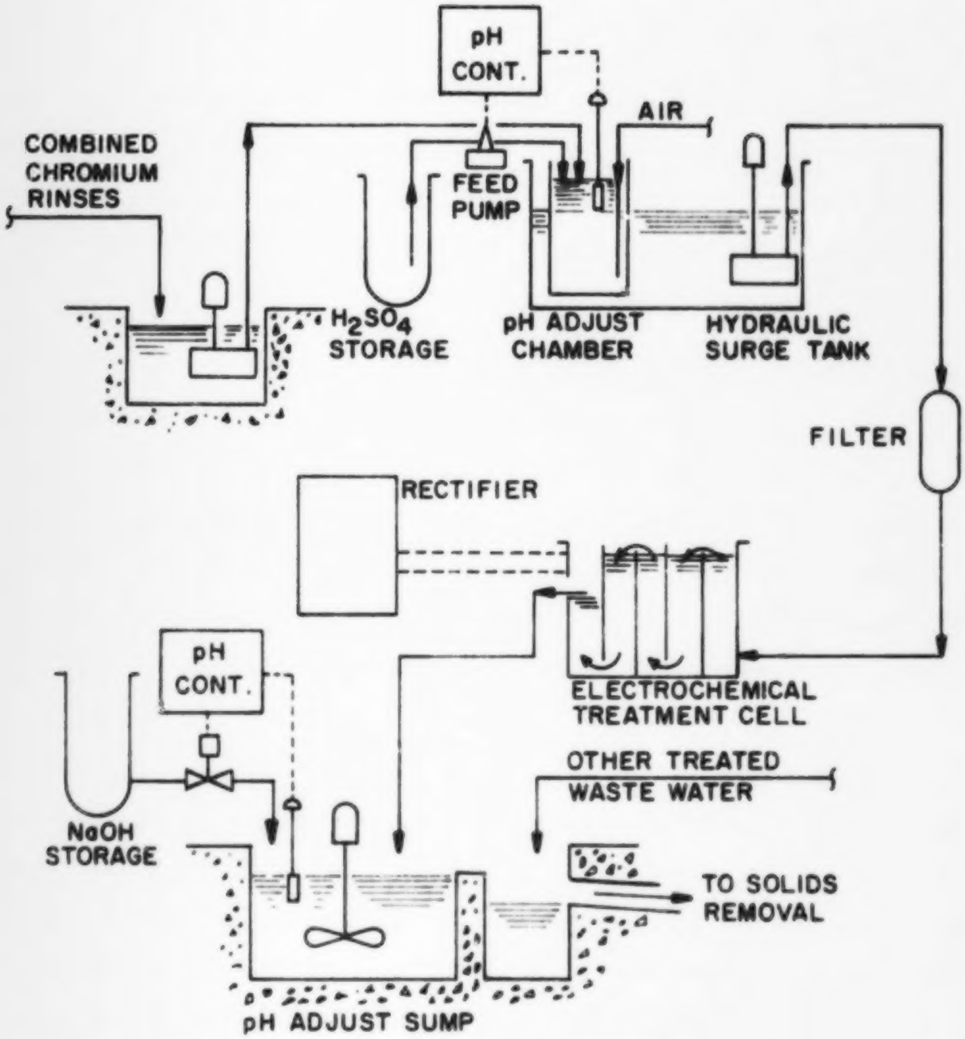

pH CONT.
AIR
COMBINED CHROMIUM RINSES
FEED PUMP
H_2SO_4 STORAGE
pH ADJUST CHAMBER
HYDRAULIC SURGE TANK
FILTER
RECTIFIER
pH CONT.
ELECTROCHEMICAL TREATMENT CELL
OTHER TREATED WASTE WATER
NaOH STORAGE
TO SOLIDS REMOVAL
pH ADJUST SUMP

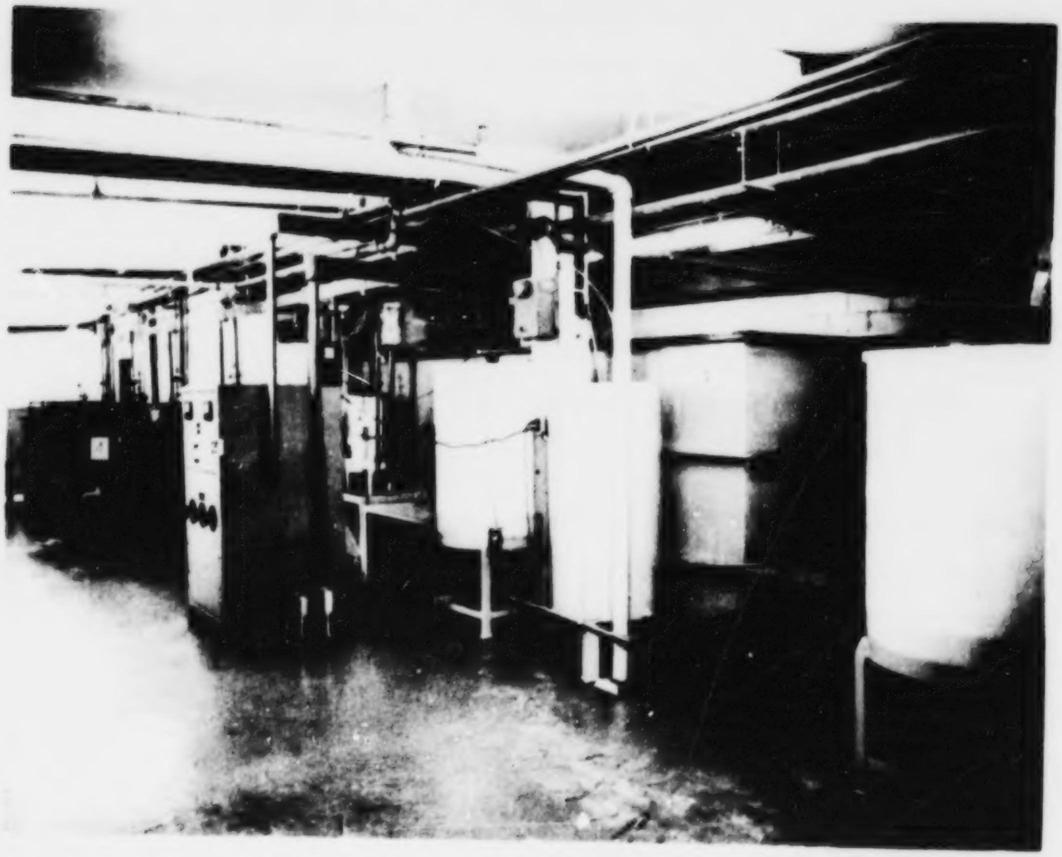
Figure 6. Chromium rinse water treatment schematic

tank. The pH is adjusted to a range of 1.5 to 2.0 for the electrochemical reduction step to follow. The rinse water thus collected in the surge tank is pumped through a filter to four electrochemical treatment units connected in parallel. As the water passes through the semi-conductive carbon bed in the cells, the electrical power supplied by the rectifier reduces the hexavalent chromium to the trivalent chromium state at the many cathode sites within the bed. At a pH of 1.5 to 2, the resulting trivalent chromium remains in solution and discharges as pretreated water from the electrochemical treatment units, draining by gravity into a sump for pH adjustment.

Final treatment of the chromium rinse water is accomplished in the chromium pH adjustment sump which is equipped with a mixer and a pH controller to add dilute caustic soda solution from a storage tank. The controller permits addition of caustic soda to maintain a pH of 8.2 in the sump. The mixer assures thorough intermixing of the chemical solutions and thorough solution washing of the pH electrode. To insure complete reduction, a small amount of reducing agent (such as sodium hydrosulfite) is mixed in with the caustic soda solution.

The treated water now free of hexavalent chromium and dissolved trivalent chromium intermixes with other treated rinse water for removal of suspended solids.

Figure 7 is a picture of the installation at New England Plating wherein the electrochemical treatment process is



1. Surge Tank
2. Filter
3. Rectifier
4. Electrochemical Treatment Cells

Figure 7. Electrochemical Reduction Installation at New England Plating Co.

being used for chromium reduction.

For chemical reduction of hexavalent chromium (refer to Figure 8), the hydraulic surge tank is converted to a reduction tank and the pump is used for solution mixing. The reduced waste water drains by gravity from an overflow weir to the pH adjustment sump, by-passing the filter and the electrochemical treatment cells. An ORP controller regulates the addition of a solution of sodium bisulfite by activating a proportional control feed pump.

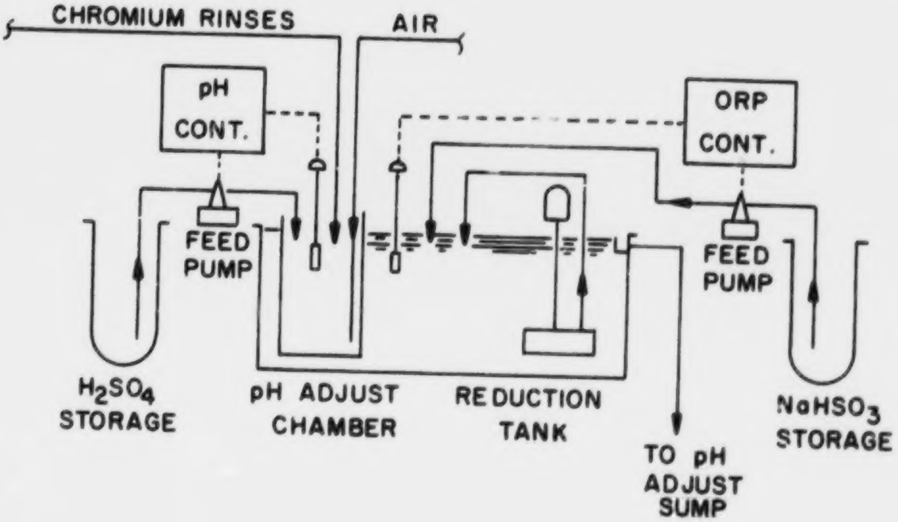

CHROMIUM RINSES
AIR
pH CONT.
ORP CONT.
FEED PUMP
FEED PUMP
H_2SO_4 STORAGE
pH ADJUST CHAMBER
REDUCTION TANK
TO pH ADJUST SUMP
$NaHSO_3$ STORAGE

Figure 8. Chemical reduction of chromium schematic

In normal operations, the following conditions prevail when the system is operating by electrochemical reduction of hexavalent chromium:

pH	1.8 - 2.1
Flow	38-150 l/min (10-40 GPM)
Cell potential	7.7 volts
Current	175 amps (at 75 l/min)

When operations are being conducted under chemical reduction of hexavalent chromium, the following conditions prevail:

pH	2.0 - 2.5
Flow	38-150 l/min (10-40 GPM)
Solution potential	+300 mv

The acid neutralization step used for final pH adjustment remains the same for either reduction process. The pH is maintained at 8.0 - 8.5 for minimum solubility of trivalent chromium hydroxide.

Cyanide Rinse Water Treatment

Figure 9 will assist in the description of the treatment system for cyanide bearing rinse waters.

The combined cyanide bearing rinse waters that have been isolated from other process water drain by gravity into a collection sump. The sump is equipped with a level control, a high level alarm and a pump for transporting the water into the cyanide rinse surge tank.

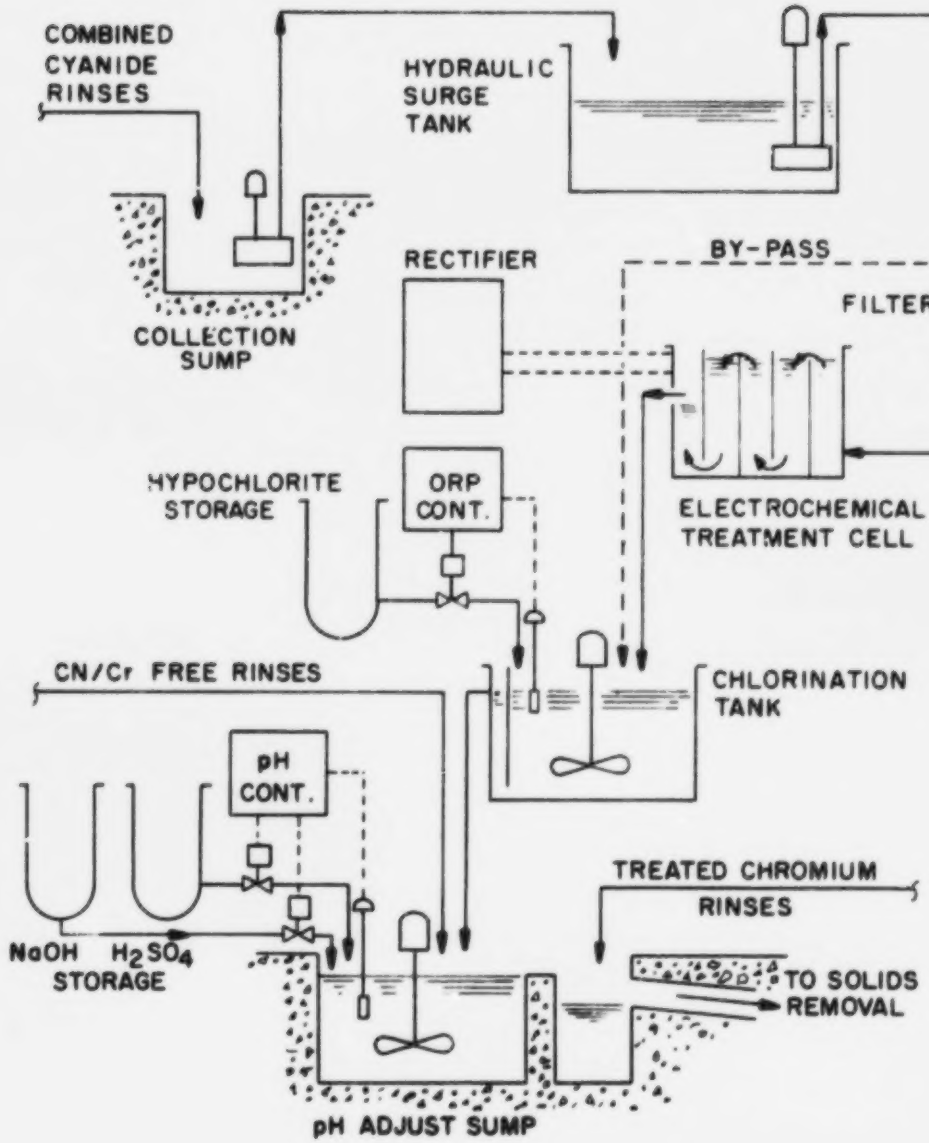

COMBINED CYANIDE RINSES
HYDRAULIC SURGE TANK
COLLECTION SUMP
RECTIFIER
BY-PASS
FILTER
HYPOCHLORITE STORAGE
ORP CONT.
ELECTROCHEMICAL TREATMENT CELL
CN/Cr FREE RINSES
CHLORINATION TANK
pH CONT.
TREATED CHROMIUM RINSES
NaOH
H_2SO_4
STORAGE
TO SOLIDS REMOVAL
pH ADJUST SUMP

Figure 9. Cyanide rinse water treatment schematic

The cyanide bearing rinse waters have a pH that is always above 10.5, and it is not necessary to adjust the pH as in the case of the chromium rinses. The rinse water thus collected is pumped through a filter to three electrochemical treatment units connected in parallel. As the water passes through the semi-conductive carbon bed in the cells, the electrical power supplied by the rectifier oxidizes the cyanide compounds at the many anode sites within the bed. The discharge from the electrochemical treatment units drains by gravity into a chemical oxidation tank which is equipped with a mixer and an ORP controller to regulate the addition of sodium hypochlorite from a storage tank. The controller permits the addition of the hypochlorite so as to always maintain a slight excess of oxidizing agent (measured as free chlorine). The mixer assures thorough intermixing of the chemical solutions and thorough solution washing of the ORP electrode.

The overflow from the chlorination step intermixes with rinse water that is normally free of cyanides and chromium compounds for final pH adjustment and precipitation of metal hydroxides. This step is performed in a sump which is equipped with a mixer and pH controller to add either dilute sulfuric acid or dilute caustic soda from storage tanks. The controller permits acid or alkali addition to maintain a pH range of 6.5 - 8.5. The mixer assures thorough intermixing of the chemical solutions and thorough washing of the pH electrode. The treated water now free of cyanide and metal ions intermixes with other treated rinse water for removal of suspended solids. The dashed line shown in Figure 9 shows how the flow can be diverted around the electrochemical treatment process when straight chemical oxidation of cyanide is desired.

Figure 10 is a picture of the installation at New England Plating wherein the electrochemical treatment process is being used for oxidation of cyanides.

In normal operations, the following conditions prevail when the system is operated in the electrochemical oxidation mode:

pH	10.5
Flow	30-115 l/min (7-30 GPM)
Cell potential	40 volts
Current	560 amps (at 115 l/min)

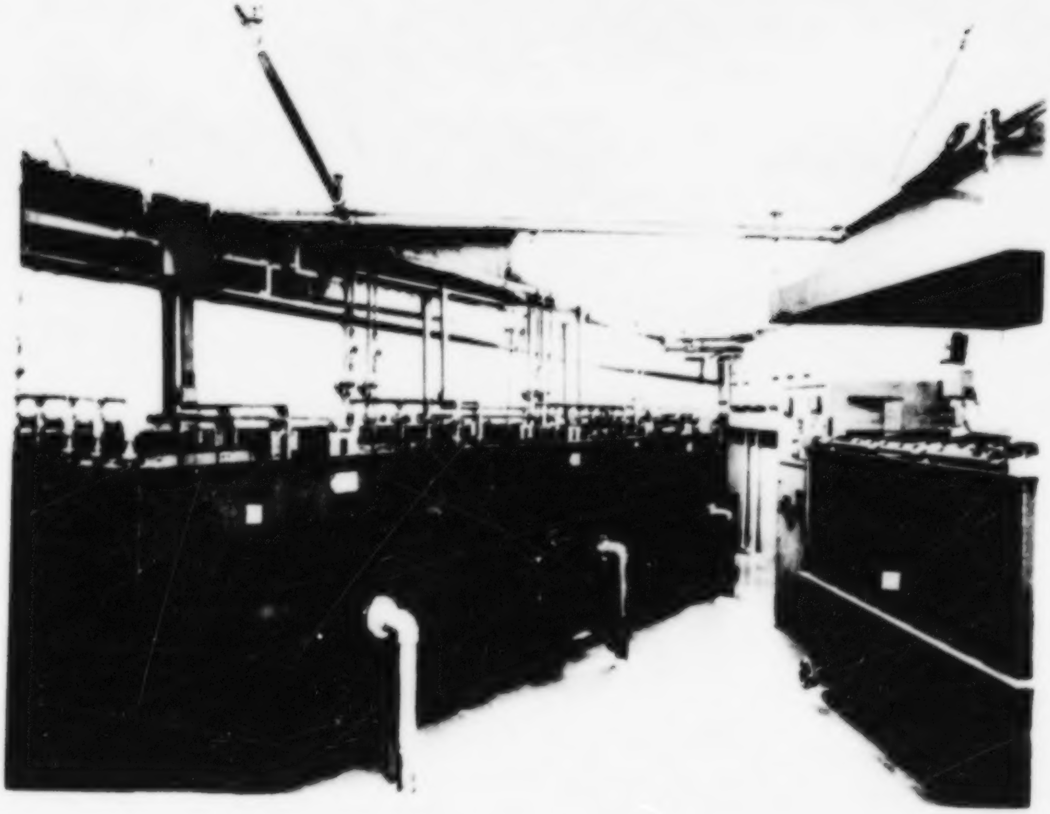
The chlorination operation that is applied whether or not the electrochemical treatment process is in use is conducted under the following conditions:

pH	10.5
Flow	30-115 l/min (7-30 GPM)
Solution potential	+550 mv

The pH adjustment step following the chlorination remains the same for either oxidation process. The pH is maintained at 6.5 - 8.5.

Electrochemical Treatment Cell Configuration

The electrochemical treatment process employed in the demonstration is based upon the concept of obtaining oxidation/



1. Electrochemical treatment cells (3) for rinse water
2. Electrolysis cell for concentrated cyanide
3. Rectifier for concentrate cell
4. Not shown, but to left: surge tank, pump, filter, and rectifier for electrochemical treatment cells

Figure 10. Electrochemical oxidation installation at New England Plating Co.

reduction reactions in a bed of inert conductive particles that are loosely packed to impart a semi-conductive nature to the bed. Potentials are maintained between particles and/or agglomerates of particles. This produces a bipolar effect of the particles (or agglomerates) and a miniature cell is developed between the particles. This multiplicity of miniature cells produces many anodic and cathodic sites within the major cell (or unit). As the waste water passes through the bed, the ionic forms in solution are subjected to very close contact with the miniature electrodes and undergo oxidation and reduction reactions. A secondary effect is believed to occur through electrolysis of the water and other chemicals present. These form oxidizing and reducing agents that are liberated into the waste water and undergo chemical reactions with the contaminants. Figure 11 depicts the semi-conductive bed concept. The bed particles are shown in Figure 12. Figure 13 is a photograph of the patented[27] cells employed in this demonstration project. Other cell configurations have come into being since the start of this project and are mentioned in Section IX.

The flow of waste water through the cells is adjusted for a maximum effective contact time within the bed. The major electrodes act as baffles and are over- and under-flowed to prevent solution from bypassing the beds. These cells have an effective bed length of 2.5 m (100 in.), and at normal flow conditions maintain a solution contact time of 20 min. If greater bed length were used to provide longer contact

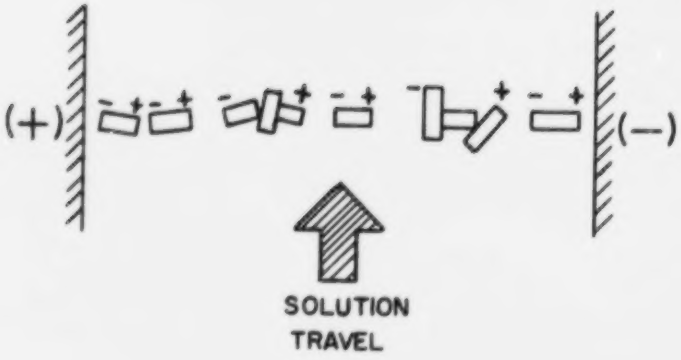
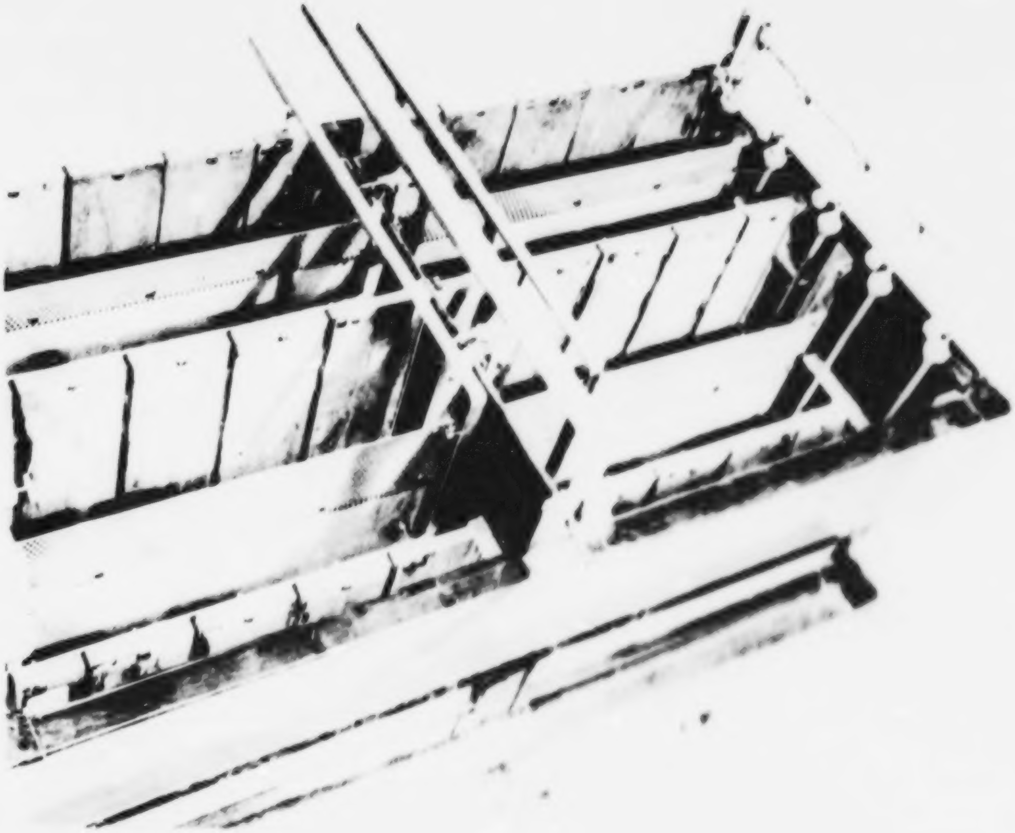

(+)
(–)
SOLUTION
TRAVEL

Figure 11. Semi-conductive bed electrolysis

Figure 12. Bed particles



1. Major Anodes
2. Major Cathodes
3. Bus Bars
4. Air Manifold
5. Solution Inlet
6. Solution Outlet

Figure 13. Electrochemical treatment cell

times, it is expected that higher levels of contaminants could be removed. The hydraulic capacity is determined by the width of the cells when anode to cathode distances remain constant at 15 cm (6 in.), as in the present case.

The cells are equipped with air manifolds at the bottom of the the individual bays so that the beds can be agitated periodically in order to flush out precipitated solids that would tend to plug the bed and restrict flow. This agitation is also used to maintain bed fluidity, as packing tends to reduce the semi-conductive nature of the cells and reduces efficiency.

Rinse Waters Free of Cyanides and Chromium Compounds

The combined rinse waters that are known to be free of cyanides and chromium compounds drain by gravity into a collection sump. The sump is equipped with a level control, a high level alarm and a pump for transporting the water into the final pH adjustment sump.

This waste water is normally acidic and is intermixed with the discharge from the cyanide rinse water treatment system in the sump. The sump is equipped with a mixer and pH controller to add either dilute sulfuric acid or dilute caustic soda from storage tanks. The controller permits acid or alkali addition to maintain a pH range of 6.5 - 8.5. The mixer assures thorough intermixing of chemical solutions and washing of the electrode.

The treated waste now intermixes with chromium treated waste water for removal of suspended solids.

BATCH WASTE TREATMENT

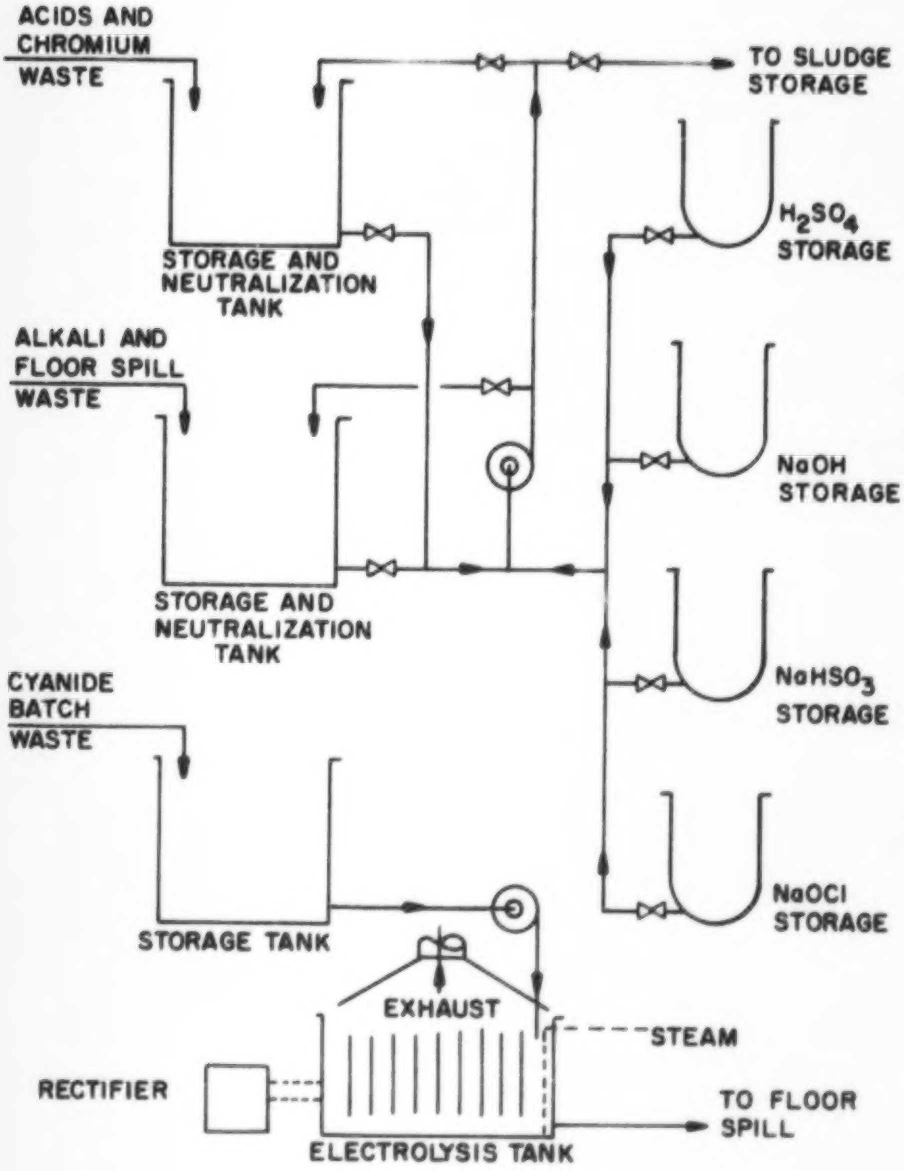
Details of the subsystems used for batch treatment of periodic batch dumps follow. A schematic flow diagram is provided as an aid to the explanation. The results of the studies conducted with these systems are to be found in Section VII, Demonstration of Treatment.

Acid and Chromium Batches

Figure 14 will assist in the description of the treatment system for acid and chromium bearing batch discharges.

Acids and spent chromate dips drain or are pumped into a collection sump for transfer to a holding and neutralization tank located in the waste treatment area. This tank is equipped with a high level alarm to alert the operator when the tank is about two-thirds full. Auxiliary equipment includes mixers and storage tanks for dilute acid, dilute caustic soda and sodium bisulfite solution.

When it is desired to treat a batch of waste, the mixer in the tank is turned on to thoroughly intermix the various dumps that have found their way into the tank. At the same time, the batch treatment pump is turned on to assist in solution intermixing. A sample is withdrawn for pH measurement and hexavalent chromium analysis. If chromium is present, reduction is required. If the pH is below 4.5, no acid



ACIDS AND CHROMIUM WASTE
TO SLUDGE STORAGE
H_2SO_4 STORAGE
STORAGE AND NEUTRALIZATION TANK
ALKALI AND FLOOR SPILL WASTE
NaOH STORAGE
STORAGE AND NEUTRALIZATION TANK
$NaHSO_3$ STORAGE
CYANIDE BATCH WASTE
NaOCl STORAGE
STORAGE TANK
EXHAUST
STEAM
RECTIFIER
TO FLOOR SPILL
ELECTROLYSIS TANK

Figure 14. Batch treatment schematic

addition is required. If the pH is above 4.5, sulfuric acid is used to lower the pH. Sodium bisulfite is slowly added until tests show the absence of hexavalent chromium. Following chromium reduction, the pH is increased by the addition of caustic soda (or other waste alkali) to precipitate the heavy metal hydroxides. The pH is normally raised to 7.5 to 8.5.

After chromium is reduced and the metal hydroxide precipitated, the treated batch is sent to the solids handling facilities for storage and sludge dewatering.

If no hexavalent chromium is present, only pH adjustment takes place.

Alkali and Floor Spill Batches

Figure 14 is a schematic presentation of the method employed for treating batch discharges from alkalis and floor spills.

The floor spill collection sump also receives all spent alkalis that are normally free of heavy concentrations of cyanides. The waste is transferred from this sump to a holding and neutralization tank located in the waste treatment area. This tank is equipped with a high level alarm to alert the operator when the tank is about two-thirds full. Auxiliary equipment provides for mixing and the addition of dilute acid, dilute caustic soda and sodium hypochlorite from storage tanks.

When it is desired to treat a batch of waste, the mixer and batch treatment pump are used to intermix the various dumps in the tank. A sample is withdrawn for analysis and pH measurement. If cyanide is found to be present, oxidation is required. If the pH is below 10.5, caustic soda is added to raise the pH for rapid oxidation. When the pH is above 10.5, chlorination of the waste is practical. Normally this process does not see high concentration of cyanide waste. Small additions of hypochlorite (either sodium or calcium) are made to the agitated waste water until a test for free chlorine is positive for at least a half hour, when all cyanide is considered to have been oxidized. After oxidation, the pH is reduced to 7.5 - 8.5 to precipitate any heavy metal hydroxides.

After cyanide oxidation and pH reduction, trace quantities of hexavalent chromium that might be present are reduced by the manual addition of sodium hydrosulfite.

If no cyanide or hexavalent chromium is present, only pH adjustment takes place.

The treated batch is finally sent to the solids handling facilities for storage and sludge dewatering.

Concentrated Cyanide Batches

Batches of concentrated cyanide waste are transferred by various means to a holding tank located in the treatment area. Conventional electrolysis at elevated temperatures is used for oxidation of free cyanides and some of the more tightly held metal cyanide complexes. Details of this electrolytic process can be found in the literature.[28-30]

The electrolytic process is used to reduce high concentrations to low levels so that final treatment can be accomplished by chemical means in the aforementioned process with a minimum amount of hypochlorite consumption.

This process operates at a temperature near the boiling point. The voltage applied depends upon the current demand of the particular batch being treated, but normally 6 volts is used. Exhaust is required.

After a given batch has been electrolyzed to the point of diminishing returns, the batch is discharged to the floor spill collection system for further treatment.

SOLIDS HANDLING

The waste treatment facility provides for the removal of suspended solids by gravity separation from flowing waste water in a tube settler. The solids resulting from settling are further concentrated by centrifugal force. Solids from batch neutralization practices are further concentrated by centrifugal force. The details of the solids handling installation are to be found in Section VIII, Solids Handling Program.

REFERENCE

27. U. S. Patent Number 3,692,661, Apparatus for Removing Pollutants and Ions from Liquids.

28. Dobson, J. Disposal of Cyanide Wastes. Metal Finishing, February 1947. p. 78-81.

29. Gray, A. G. Practical Methods for Treatment of Plating Room Wastes. Products Finishing, August 1950. p.68-84.

30. Oylar, R. W. Disposal of Waste Cyanides by Electrolytic Oxidation. Plating, April 1949. p. 341-342.

SECTION VII

DEMONSTRATION OF TREATMENT

GENERAL

The various studies being reported were designed to demonstrate the economics and reliability of the various subsystems employed. Tests were conducted to characterize each separate waste stream to provide more data on the amount of cyanide and chromium compounds being treated, as it was anticipated that changes in plating practices would result in quantities that varied from the design basis reported in Section VI. Further tests were conducted to widen the applicability of data to others electing to use this electrochemical treatment process.

The systems described earlier (Section VI) provide means for operating the treatment facility under either chemical or electrochemical mode on the identical waste being generated. Exhaustive chemical processing was not conducted, as these techniques are amply described in the technical literature. The studies of the chemical treatment steps were of adequate depth to insure process reliability and of sufficient length to obtain reasonably accurate operating cost data for comparison purposes.

Further data was obtained to explain the roles of several electrochemical process variables and their impact upon the specific process under study.

The effluent character and quality with regard to the primary contaminant are being reported for the subsystems and some combination of subsystems, and, of course, for the total treatment plant.

The results of the tests and studies are found under the following divisions of this section of the report: chromium treatment, cyanide treatment, wastes free of cyanide and chromium compounds. Similar information relative to solids handling is reported in Section VIII of this report.

CHROMIUM TREATMENT

Chromium bearing rinses were processed with the semi-conductive bed electrolytic process for reduction of hexavalent chromium to the trivalent state. Subsequent hydroxide precipitation was achieved using sodium hydroxide for pH adjustment. Also, the same waste was reduced with bisulfite and the same techniques employed for subsequent pH adjustment.

Batch treatment was employed for reduction of spent solutions containing hexavalent chromium. Electrolysis was also used on some spent chromium bearing batch wastes.

Characterization of Waste Waters

The original design basis for treatment of chromium bearing rinses considered a hydraulic loading of 150 l/min (40 GPM) and hexavalent chromium concentrations in the order of magnitude of 120 mg/1. Upon completion of water conservation efforts and deletion of some low volume metal finishing processes, flowing rinses totaled approximately 75 1/min (20 GPM). During the twelve months of study on this system, daily grab samples of the raw waste were monitored for $[Cr^{+6}]$. The concentration values do not fit a normal frequency distribution curve. However, the log $[Cr^{+6}]$ does fit the curve and is shown in Figure 15. Data from this histogram and factors from standard probability tables were used to construct the curve in Figure 16 which depicts the probability of seeing any given concentration in the rinse water. Analysis of this data shows that during 90 percent of the time, the concentration was less than one-half of the design criteria. During one-third of the time, the concentration was less than 10 percent of the design criteria.

In view of the concentration variations that could occur within a given day and the potential error in drawing conclusions solely from analysis of one daily grab sample, hourly grab samples were taken on two separate days. The results are shown in Table 4. It was felt that no severe anomalies existed that would prohibit use of the statistical data from grab samples in subsequent calculations.

The pH of the raw waste was monitored over a three-week period. While the rinse water was always acidic, the pH varied from 1.7 to 6.3. With effective pH control of the raw waste prior to electrolysis, the pH range was narrowed to 1.7 - 2.3.

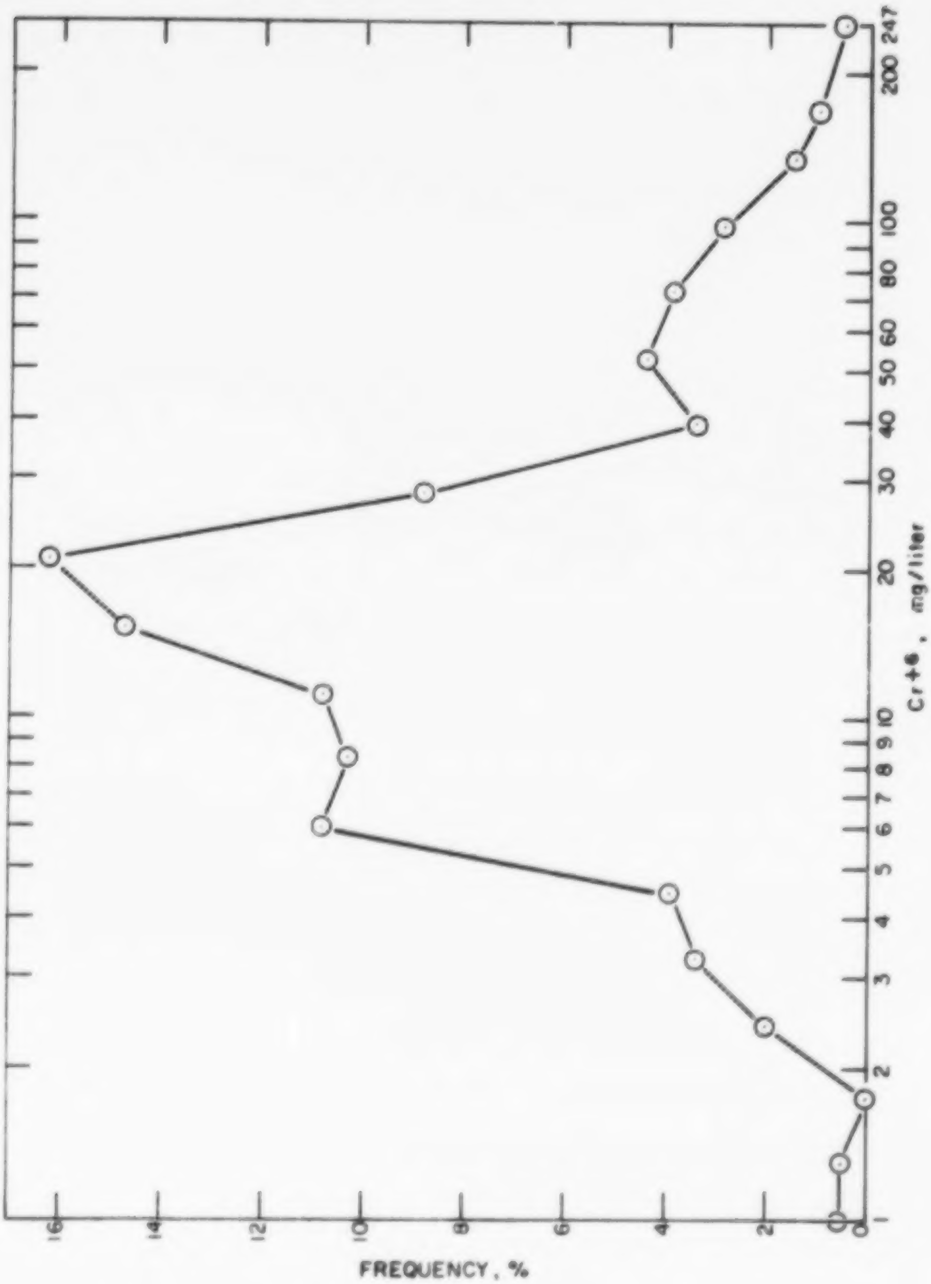


Figure 15. Hexavalent chromium in raw waste

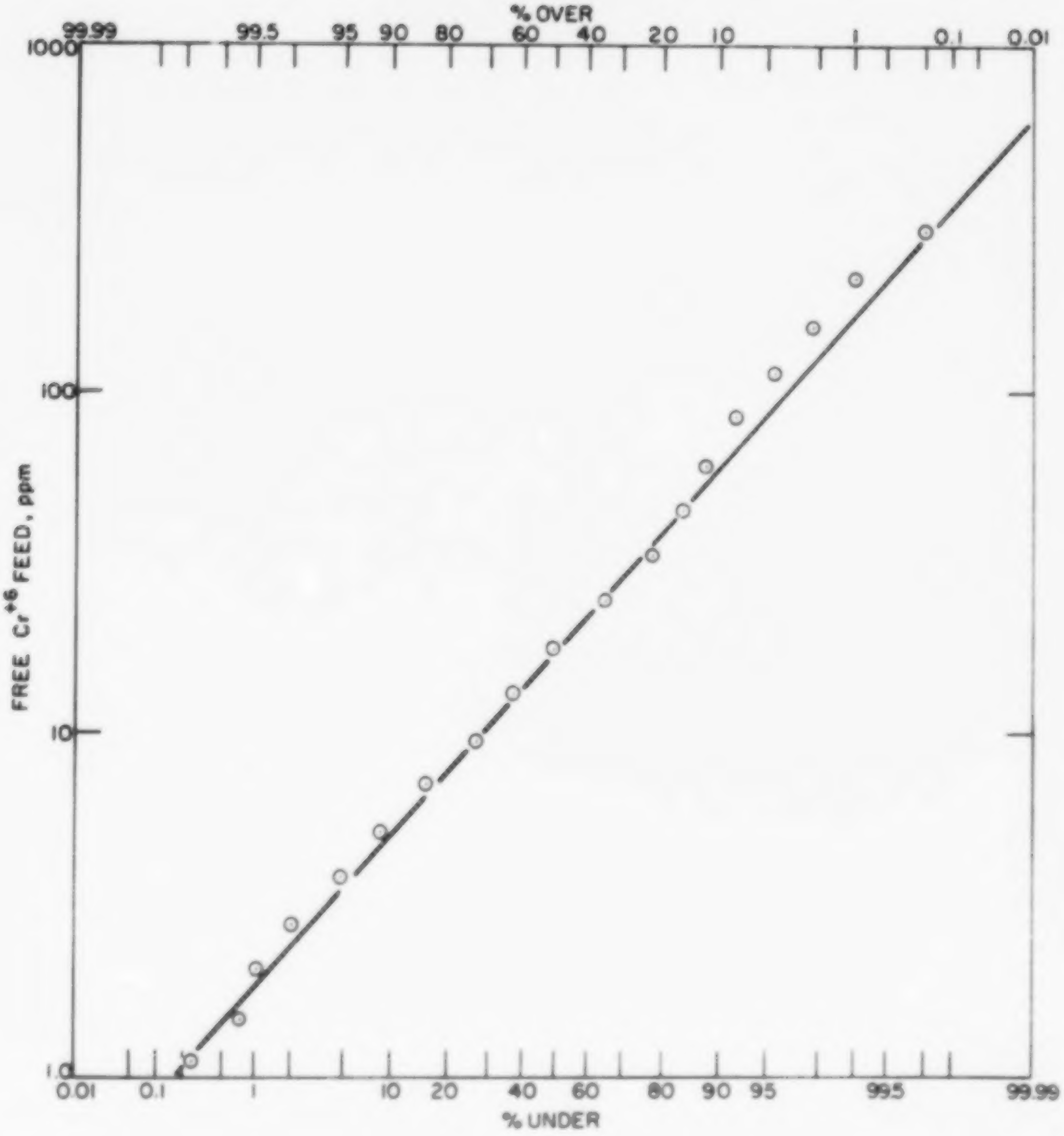


Figure 16. Concentration of hexavalent chromium in raw waste - probability curve

Table 4. HEXAVALENT CHROMIUM IN ISOLATED RAW WASTE DURING PRODUCTION DAY

Time	milligrams/liter 4/11/73	 2/12/73
0800	11.0	9.9
0900	5.5	6.6
1000	5.5	9.9
1100	3.3	13.2
1200	4.4	11.0
1300	4.4	11.0
1400	5.5	13.2
1500	6.6	22.0
1600	4.4	24.2
1700	6.6	20.9
1800	13.2	24.2
1900	12.1	20.9
2000	--	18.9
2100	18.6	17.6
2200	17.6	17.6

Batch waste containing hexavalent chromium can be characterized as amounting to 9000 l (2350 gal.) per week with an average concentration of 430 mg/l of hexavalent chromium. During the demonstration period, two batches of chromium containing waste were treated that were abnormal. With the deletion of several process operations, a chromic acid anodizing solution (at 100 g/l of CrO_3) and a chrome plating solution (at 240 g/l of CrO_3) required batch treatment. These two occasions, while providing sludge for solids handling studies, contributed little to studies in this section of the report and were not used in characterizing the waste water.

Rinse Treatment

Rinse waters containing hexavalent chromium were processed through the electrolytic cell and by chemical reduction for cost determination and comparison. Tests were also conducted to determine the maximum hexavalent chromium concentration allowable in the raw waste for full and effective utilization of the electrolytic process.

Preliminary pH Adjustment Step -

Due to wide pH variations in the raw waste water (1.7 to 6.3), problems caused by heavy metal hydroxide precipitation within the bed were experienced initially. Trivalent chromium hydroxide precipitated as well as other metals, such as iron and zinc. These solids were retained in the bed at the higher pH values and increased the back pressure of the system causing the individual bays within the cell to overflow. With the waste water overflowing bays and bypassing the bed, significant reduction in overall cell efficiency was experienced.

Adjustment of the pH to values in the range of 1.8 to 2.1 resulted in a modest sulfuric acid consumption and a slightly higher power consumption. However, within this range a bed fluidity was maintained which minimized cell maintenance and produced consistent results. In addition, the filter cartridge replacement was reduced to three changes every two months from at least three changes a week. Adjustment of the pH to a value lower than 1.8 was not considered desirable in cells of the design used in this demonstration, as the life of the graphite anodes drops off with lower feed pH levels. At the established pH values, the graphite anodes have a useful life of 1.5 years.

The acid consumed during electrolytic reduction for a continuous 75 l/min (20 GPM) flow was 0.84 kg (1.84 lb) per hour. To obtain high efficiencies with bisulfite reduction, a pH range of 2.0 - 2.5 was used when operating in the chemical reduction mode. Sulfuric acid consumption was 0.71 kg (1.57 lb) per hour for the same averaged flow rate.

Electrochemical Reduction Step -

Four cells were used in parallel, each having a nominal capacity of 38 l/min (10 GPM). Since the flow was one-half of this value, the system operated at maximum capacity in a pulsing ON/OFF mode. Each cell was used 50 percent of the time as the level of accumulated waste water in the surge tank rose and fell. Samples of rinse water before and after electrolysis were analyzed for hexavalent chromium and the pH was measured. At the same time, power consumption (voltage and amperage) was recorded and the flow measured.

Periodically, air was introduced into the bottom of the cell sections to re-suspend the bed so as to keep the carbon particles from compacting during treatment. Occasionally water was introduced in place of air to aid in flushing occluded particles from the bed. These fines were for the most part particles that had fallen from the graphite anodes as they eroded. Some carbon fines were observed during cleaning with water which were believed to have come from bed attrition. Bed attrition, which amounted to 2.5 percent per month, is caused by particles abrading against each other and against the partitions.

The 2.5 m (100 in.) of travel through the bed provided ample time (20 min.) for virtually complete reduction of hexavalent chromium. Flows higher than 150 l/min (40 GPM) could not be processed due to the cell design. Lower flow rates did not produce any improvement in the quality of the cell discharge.

It was recognized that activated carbon is a good adsorber for hexavalent chromium. The carbon for the bed was primarily selected for its size, shape and hardness. When compared for adsorption with other carbons, it was obvious that better adsorbing properties were available if this property were the governing performance factor. Since it was felt that the primary factor was electrolytic action, only minor attention was paid to the adsorption phenomenon. There were periods during the demonstration when hexavalent chromium bearing waste water passed through the cell with D.C. power off. In the absence of applied voltage, the level of hexavalent chromium in the cell discharge gradually increased. When power was again applied, the concentration level returned to the low values obtained prior to power interruption.

The amount of power applied to these cells using a 15 cm (6 in.) spacing between major opposing electrodes was sufficient to produce a slight amount of gassing at the major cathodes. Higher voltages apparently produced little if any improvement in reduction efficiency. At the normal operating voltage, the amount of current drawn by the cells was dependent upon the pH and the chromium concentration in the waste water. In addition, as the bed became more compact when the time between bed agitation was extended an increase in the amount of current consumed was observed.

The amount of operating labor required by the electrochemical treatment process during the 12-month study period was 100 hours. Approximately half of this was consumed in preparing the dilute sulfuric acid solution, one-fifth each in bed maintenance and filter tube replacement. Maintenance labor during this period amounted to 70 hours. One-third of this amount was devoted to anode replacement, with an equal amount directed towards delivery pump repairs.

During the first six months of 1973, analysis of the discharge data shows:

57% of the time, cell discharge was 0.05 mg/l or less
75% " " " " " " 0.08 " " "

83% of the time, cell discharge was 0.10 mg/l or less
98% " " " " " " 0.30 " " "
100% " " " " " " less than 1.0 mg/l

The weighted average discharge from the cell was 0.06 mg/l. With an average feed concentration of 17 mg/l, this amounts to an average removal efficiency of 99.7 percent. Higher efficiencies were realized when peak loadings greater than 100 mg/l were observed in the raw waste. Even with significant variation in feed concentration (see waste characterization information), there was virtually no change in cell discharge concentration.

To insure that instantaneous daily observations were indicative of results throughout the day, hourly samples throughout a given production day were monitored. The concentrations in the cell discharge are listed in Table 5.

Power consumption during this period averaged at 390 amperes and 7.8 volts. A prolonged period of stability was demonstrated with the current range being 350 - 455 amperes (with monthly averages of 380 - 425) and the applied voltage range being 7.5 - 8.0 volts (monthly averages 7.7 - 7.8). The average kilowatts consumed were 3.0 (monthly averages 2.9 - 3.3).

A graph of the power consumed per kilogram of CrO_3 reduced as a function of the concentration of feed is shown in Figure 17. With the obvious economic advantage of the process for higher feed concentrations, additional tests were run at a

Table 5. HEXAVALENT CHROMIUM IN ELECTROCHEMICAL CELL DISCHARGE DURING PRODUCTION DAY

	(milligrams/liter)	
Time	4/11/73	2/12/73
0800	0.07	0.04
0900	0.05	0.00
1000	0.025	0.02
1100	0.055	0.02
1200	0.05	0.07
1300	0.06	0.025
1400	0.04	0.025
1500	0.05	0.04
1600	0.055	0.03
1700	0.05	0.02
1800	0.055	0.025
1900	0.03	0.015
2000	--	0.02
2100	0.06	0.01
2200	0.045	0.025

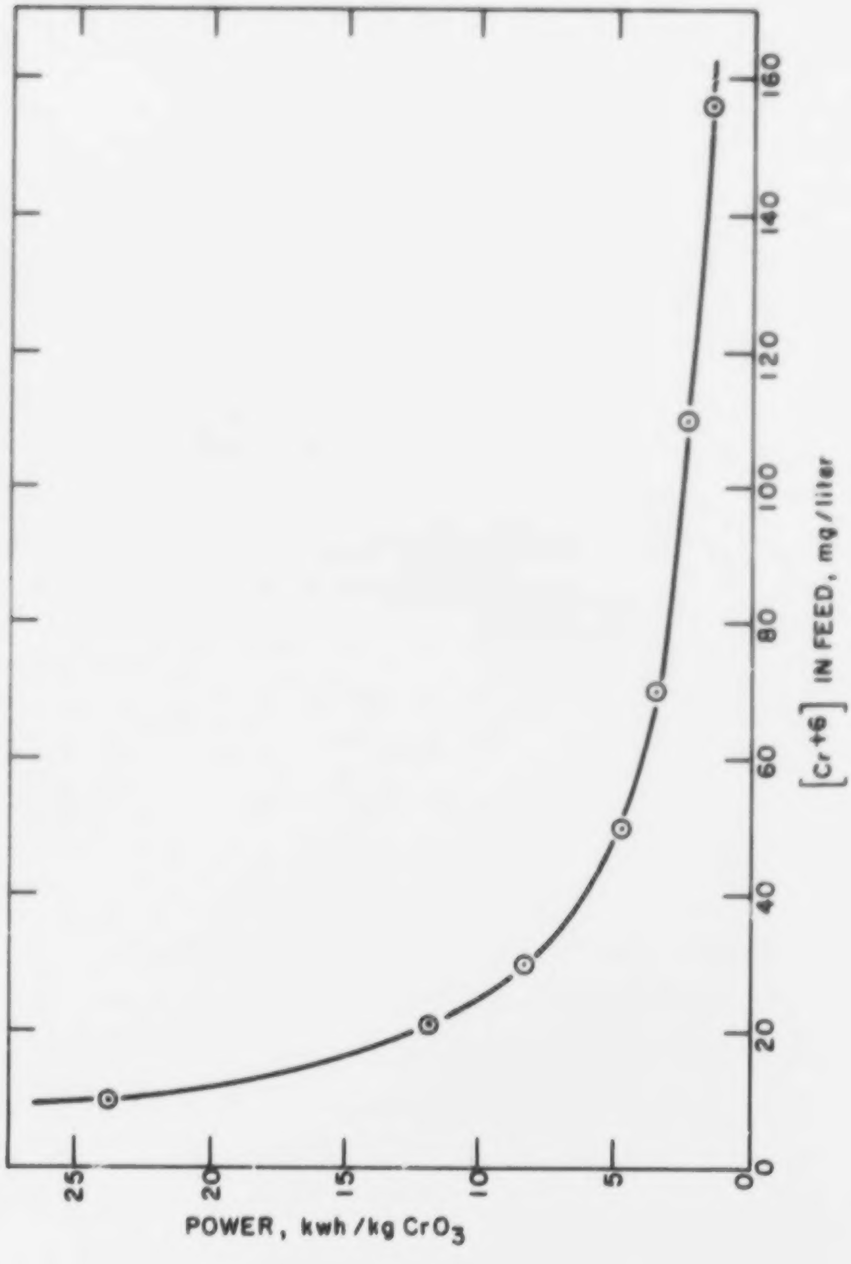


Figure 17. Power consumption for chromium reduction as a function of feed concentration

later date to determine the tolerance of these specific cells for hexavalent chromium loading.

Chemical Reduction Step -

A series of production evaluations of the chromium treatment system when operated under a mode for chemical reduction of hexavalent chromium with acidic sodium bisulfite were conducted to establish cost factors for comparison purposes.

Early evaluations were directed towards determining the optimum operating technique to meet the same quality criteria demonstrated by the electrochemical reduction process. It was realized that the equipment to be used was less than ideal, with improvements possible in the intermixing of the reducing agent and the waste water being treated. With less than perfect mixing, the ORP probe location took on greater significance. It was also recognized that the turbulence produced by the system undoubtedly caused oxygen to be entrained in the water and would account for some bisulfite consumption.

During February of 1974, over 450,000 l (120,000 gal.) of waste water was processed during a two-week period following preliminary tests to optimize the system.

The pH was controlled in a range of 2.0 to 2.5 by the addition of dilute sulfuric acid. Retention time in the reduction tank was 100 minutes. The hexavalent chromium concentration was approximately 20 percent less than average condition when the electrochemical treatment was accomplished.

Operating labor showed a 70 percent increase over that required for the electrochemical process. Of the 170 hour/year, better than half was consumed in preparing the bisulfite solution. Maintenance labor was predicted to be 70 percent of that realized by the electrochemical process.

In order to achieve the same quality of reduction, it was necessary to add an excess of bisulfite to the waste; 2.7 kg (5.95 lb) of $Na_2S_2O_5$ was consumed for each kilogram (2.2 lb) of CrO_3 reduced. This amounts to 1.9 times the theoretical amount.

Precipitation Step -

Sodium hydroxide was used to adjust the pH of the reduced waste to a range of 8.0 to 8.5. The retention time in the neutralization sump was 24 minutes under average conditions.

Operating labor, which for the most part was used to prepare the dilute alkali, amounted to 100 hr/yr. Maintenance labor consumed one-fourth that amount.

Sodium hydrosulfite ($Na_2S_2O_4$) was added daily in small quantities to the alkali to reduce any hexavalent chromium escaping the electrolytic cells; 6.8 kg (15 lb) per year was the minimum feed rate established to consistently produce the desired level of hexavalent chromium in the chromium system discharge. When bisulfite reduction was in use, the excess sodium bisulfite eliminated the need for this hydrosulfite addition.

The efficiency of this step when monitoring hexavalent chromium in the discharge is exhibited by:

57% of the time, discharge was 0.03 mg/l or less
75% " " " " " 0.05 mg/l " "
96% " " " " " 0.10 mg/l " "
100% " " " " " 0.30 mg/l " "

Chromium Tolerance Tests

It was realized that the specific cells being used for rinse water treatment provided excess capacity for chromium reduction. It was also recognized that chemical costs for chromium reduction in batch treating spent chromate solutions were higher than desired. A series of experiments were conducted to establish the maximum concentration allowable in the raw waste being fed into the electrochemical treatment cells that would be consistent with the quality desired in the effluent. It was expected that levels could be reached which would permit electrochemical treatment of spent chromate dips when added to the rinse water.

Chromic acid was prepared in a small tank adjacent to the electrochemical cells and metered into the incoming raw waste. Various feed concentrations were selected to determine the tolerance level for these cells and to determine the rate of removal as an aid for future cell design.

Based upon the data obtained, it is believed that these specific cells (2.5 meters of bed length) can tolerate a feed concentration of 150 mg/l and continue to produce an acceptable discharge (less than 0.2 mg/l). This results in New England Plating being able to discharge 85 percent of the spent chromate dips directly into the rinse water system, with the level always remaining below the critical concentration. Highly concentrated chromate dips (the remaining 15 percent) can be metered into the rinse water to further maximize utilization of the electrolytic system.

At feed concentrations approximating 150 mg/l, power consumption was 4 kilowatts when operating at maximum hydraulic capacity. At this cell loading, 1.47 kwh per kilogram of CrO_3 was realized. This compared favorably with 14.5 kwh/kg which represented the average conditions while processing normal rinse water.

By selecting specific points for analysis that were along the path of solution travel through the bed, additional data became available to monitor the rate of reduction of hexavalent chromium as a function of concentration. With feed concentrations in the range of 220-250 mg/l, 145 mg/l per meter of travel was obtained. When in the range of 160-180 mg/l, 90 mg/l per meter of travel was obtained. At a range of 60-140 mg/l, 40 mg/l per meter of travel was obtained.

BATCH TREATMENT

During the study period, batch treatment of collected waste acid and chromate dips averaged one batch per week. Sodium bisulfite was added at low pH until a slight excess of reducer was present (500-750 mg/l excess). An average of

15.4 kg (34 lb) of anhydrous sodium bisulfite ($Na_2S_2O_5$) was used for each batch. Labor claims for operating and analytical labor amounted to 1¼ hours per batch.

CYANIDE TREATMENT

Cyanide bearing rinses were processed with the semi-conductive bed electrolytic process for oxidation of cyanide to less harmful species. Following the electrolysis treatment, alkaline chlorination was employed to remove residual cyanides amenable to chlorination that might escape the electrolytic oxidation. The electrolytic process was by-passed to obtain operating cost data with only chlorination for comparison purposes.

Batch treatment of spent cyanide bearing process solutions and spill water was accomplished with electrolysis for concentrated wastes and alkaline chlorination for dilute wastes.

Characterization of Waste Waters

The original design basis for treatment of cyanide bearing rinses considered a hydraulic loading of 115 l/min (30 GPM). and cyanide concentrations in the order of magnitude of 30 mg/l. Upon completion of the water conservation efforts and other process changes, the flowing rinses totaled approximately 75 l/min (20 GPM). From February 1973 to February 1974, daily grab samples of the raw waste were always monitored for cyanides amenable to chlorination and for approximately one-fourth of the time for total cyanide. Figure 18

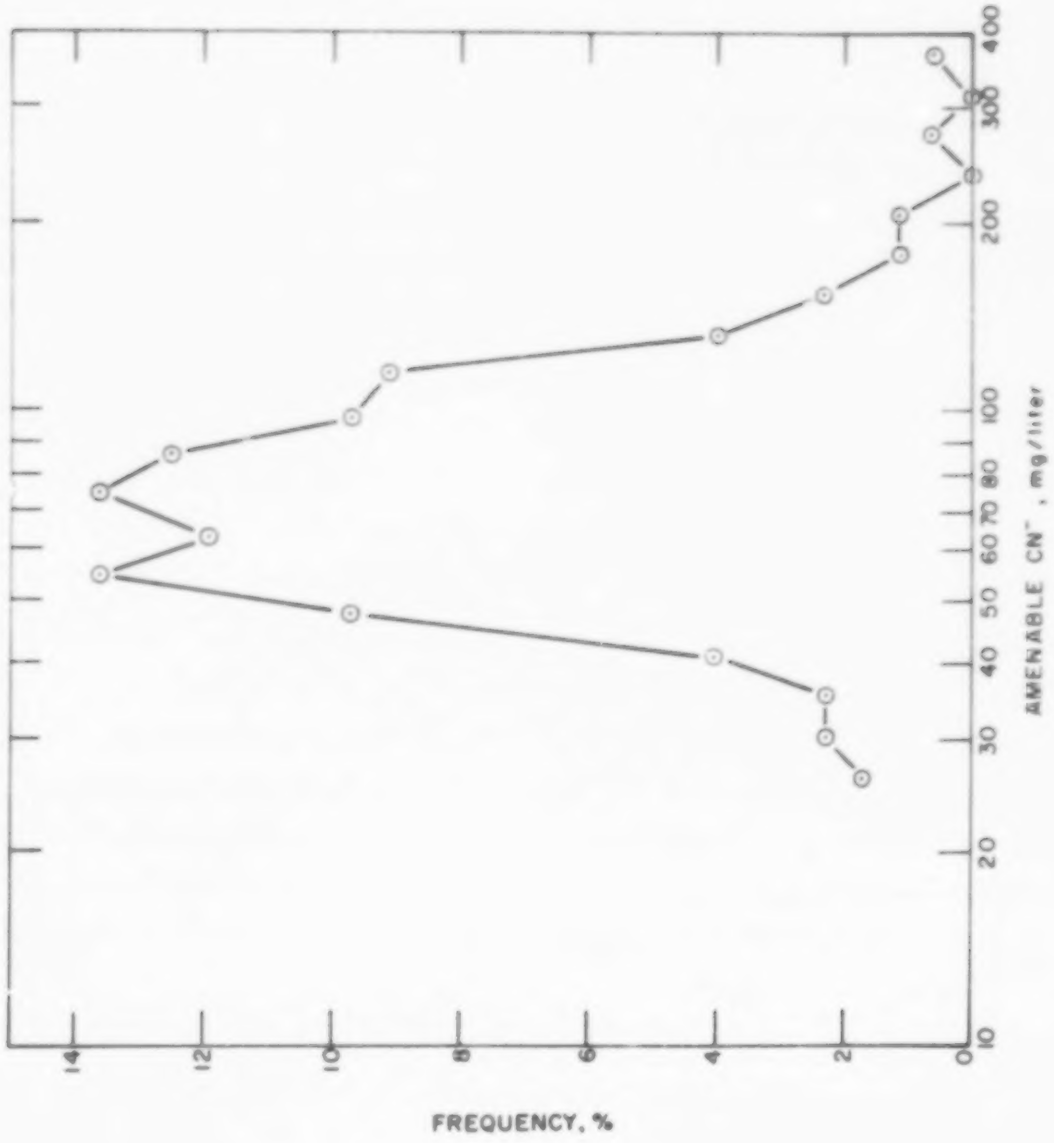


Figure 18. Cyanides amenable to chlorination in raw waste

shows the log $[CN_A]$ as a normal frequency distribution curve. Data from this histogram and factors from standard probability tables were used to construct the curve in Figure 19 which depicts the probability of seeing any given concentration in the rinse water. Analysis of the data shows that for 98 percent of the time, the concentration was above the design criteria. During one-third of the time, the concentration was more than 300 percent of the design criteria.

As in the work on the chromium system, periodic grab samples were taken on a day considered typical for cyanide processing. The results are listed in Table 6. Again, it was felt the statistical data from grab samples could safely be used in subsequent calculations.

Monitoring of the pH during the twelve-month period showed a consistent range of 11.0 to 12.0 with only six excursions to the range of 10.5 to 11.0 and two above 12.0.

By multiple regression analysis, a relationship was established between cyanides amenable to chlorination and the corresponding total cyanide value. This curve, Figure 20, is shown to be linear except at high values.

Batch cyanide wastes collected for treatment can be characterized in two general groups. Highly concentrated waste from dumped process solutions averaged 570 l (150 gal.) per week at concentrations in the range of 30-50 g/l (4-6.7 oz/gal.). More dilute waste generated from floor spills, maintenance cleaning, etc., had volumes in the range of 15,000 l

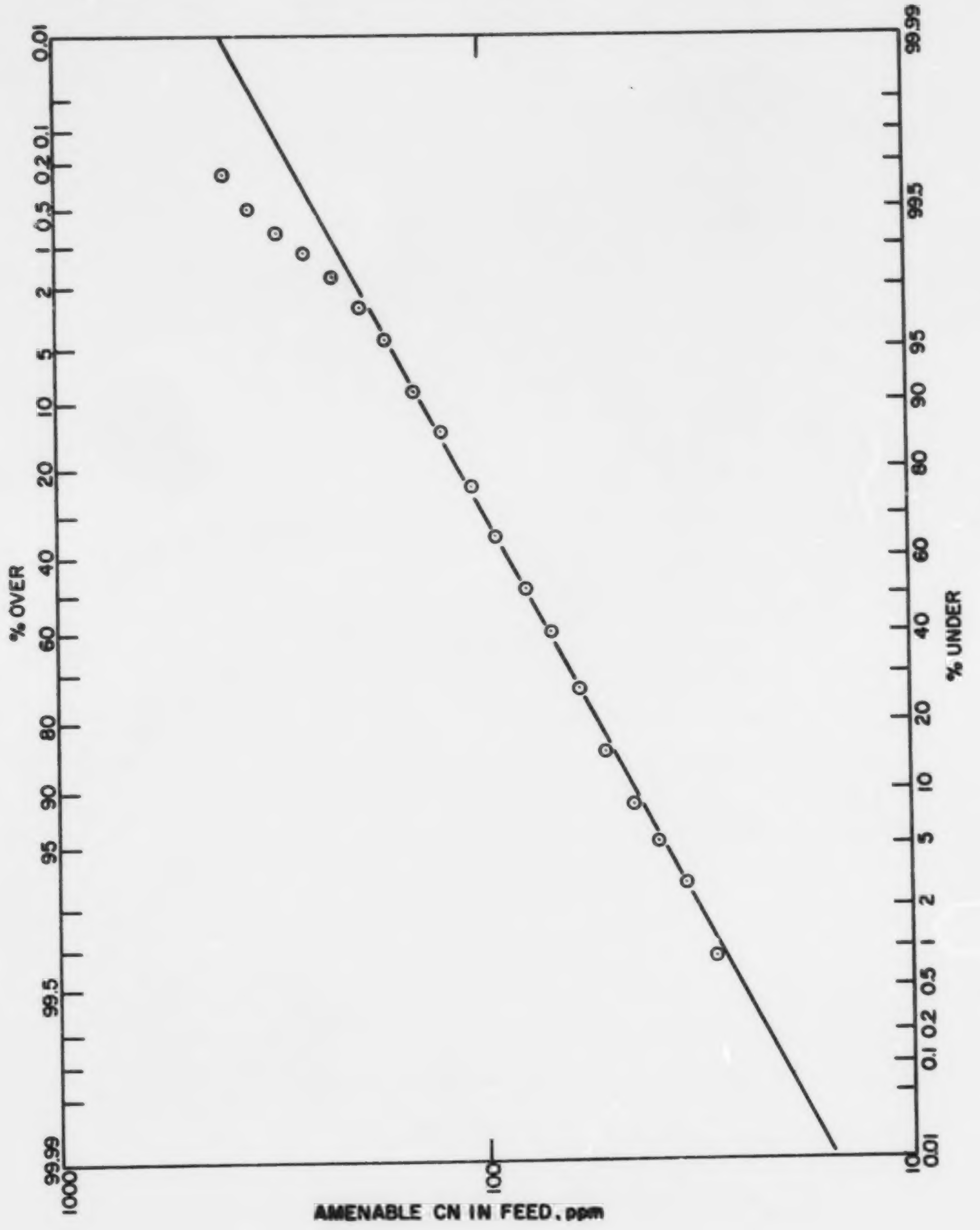


Figure 19. Concentration of cyanides amenable to chlorination in raw waste - probability curve

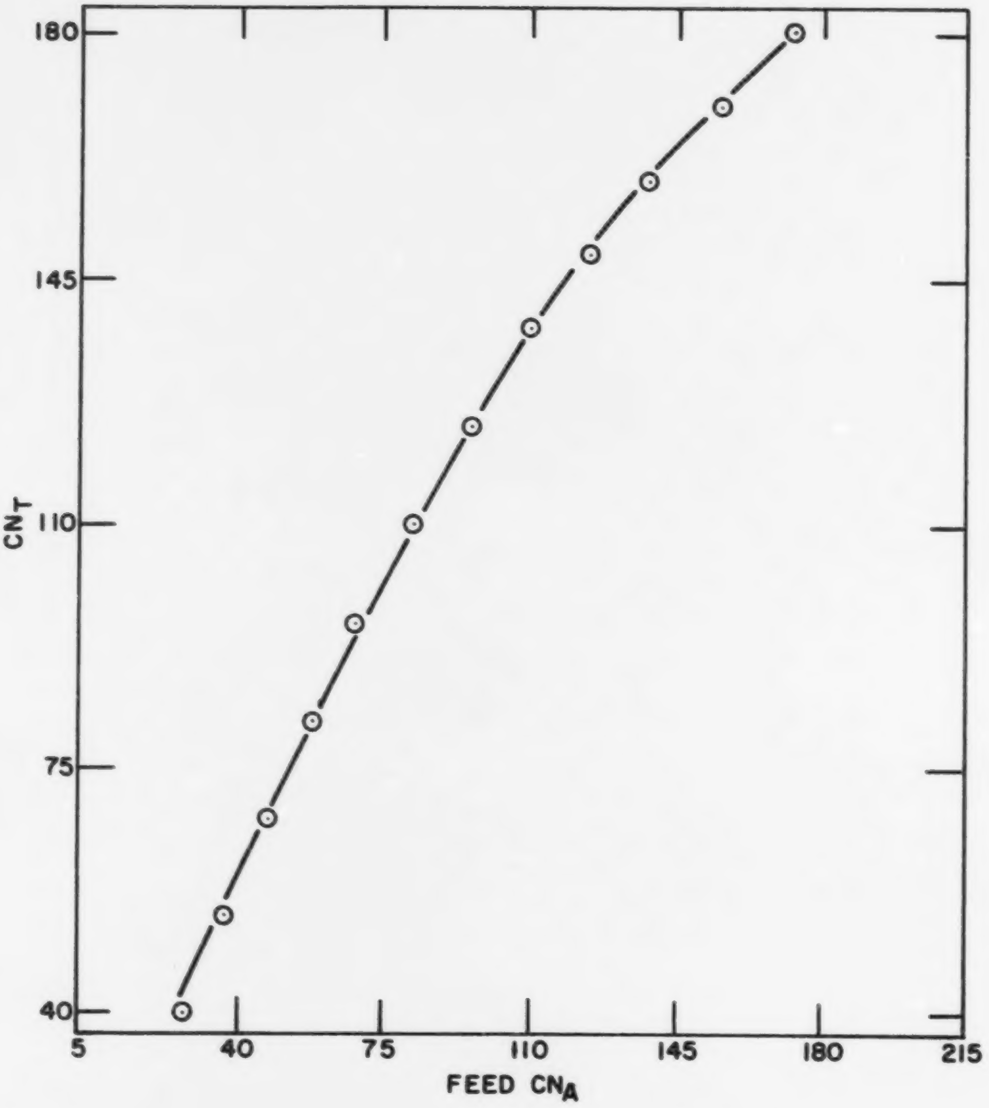


Figure 20. Total cyanide vs cyanides amenable to chlorination

(CN_T: total CN; CN_A: amenable CN)

Table 6. CYANIDE IN ISOLATED RAW WASTE DURING PRODUCTION DAY

	(milligrams/liter)	
Time	CN_A	CN_T
0815	--	85.3
0915	--	61.1
1015	83.1	111.8
1115	65.3	90.0
1215	52.1	71.8
1315	59.9	81.6
1415	47.2	75.8
1515	86.1	103.9

(CN_A: amenable; CN_T: total)

(4000 gal.) per week with concentrations normally in the neighborhood of 100 mg/l. Occasionally this more dilute waste contained 2 - 3 g/l (0.25 - 0.40 oz/gal.).

Rinse Treatment

Rinses containing cyanide were processed under varying cell potentials to optimize the electrolytic process. Prolonged evaluations at what were considered to be optimum conditions were conducted to establish quality of treatment and cost data. Further analysis was conducted in an attempt to determine the reaction products of the electrolytic process.

Role of pH -

The pH of the combined cyanide rinses was at all times above 10.5, the minimum considered safe for chlorination, and normally in the range of 11.0 to 12.0. Previous experience had shown no improvement in electrolytic oxidation by using higher (or lower) pH values.

It was noted that a drop in pH of about 0.5 was realized as the waste passed through the electrolytic cells.

Electrochemical Oxidation Step -

Three cells were used in parallel, each having a nominal capacity of 38 l/min (10 GPM). Since the flow was two-thirds of this value, the system operated at maximum capacity in a pulsing ON/OFF mode. Each cell was used 67 percent of the time as the level of accumulated waste water in the surge tank rose and fell. Samples of the rinse water before and after electrolysis were analyzed for total cyanide and cyanides amenable to chlorination, and of course the pH was measured. At the same time, power consumption was recorded and flow measurements made.

As was found during operation of chromium reduction units, oxidation cells periodically required air to re-suspend the bed to prevent compaction and a corresponding reduction in treatment. Water was used to augment the air and to aid in flushing solids from the bed. At the higher pH, characteristic of the cyanide rinse water, less graphite and bed attrition were noted than with the low pH waste. A four-year life was estimated for the anodes in this service. Bed consumption was calculated to be 1.0 - 1.5 percent per month.

The flow rate used in the demonstration provided a 20 minute retention time. Longer dwell times did not appreciably improve the oxidation. In fact, too slow a flow resulted in the liquid developing localized points of high flow and in reality a lower contact time in the bed is realized.

Carbon is known to be an effective adsorber of cyanide. Initial results with the electrochemical cells containing a new carbon bed can be misleading as the dominant mechanism of cyanide removal is adsorption. According to theory, the amount of a component adsorbed depends upon the concentration in the mass of the solution. Following periods of high concentration of waste being processed (and greater adsorption taking place), if more dilute waste is processed, desorption activity takes place. It was demonstrated under this condition that more cyanide was being discharged than was entering the system. Obviously, the adsorption phenomenon was dominating the results. To insure complete adsorption, waste was passed through the cell for a sufficient period (longer than 200 hr) so that the discharge concentration was equal to the inlet concentration. At this point, current was applied. A steady decrease in cyanide concentration in the discharge was observed. When a steady state condition existed, data was taken for cell efficiency.

A definite relationship exists between applied voltage (and increase in current) and cell efficiency as shown in Figure 21. The voltage generally used in this demonstration was 40 v., a value believed to optimize economies. At this

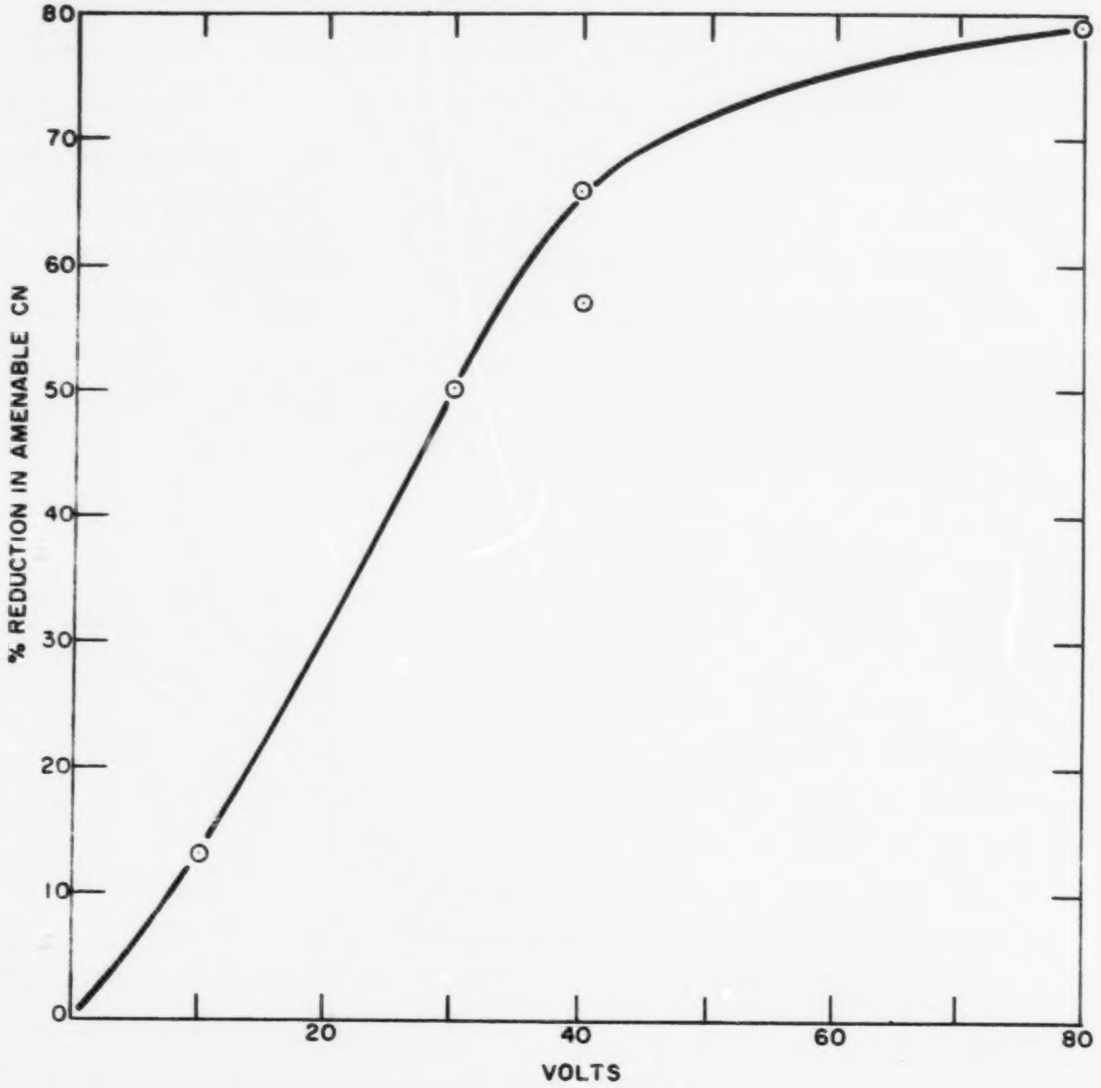


Figure 21. Cyanide oxidation efficiency as a function of applied voltage

applied voltage, 60-70 percent of the cyanide entering the cell was oxidized. This removal rate was consistent for many months, and was maintained over a fairly wide range of feed concentration. It was concluded that lower discharge levels could be reached with a large cell having a length of travel greater than the 2.5 m (100 in.) used in this demonstration.

Electrical power expended during the demonstration period averaged 22.4 kw (560 amperes at 40 volts). Based upon the average amount of cyanide removed, power consumption has been calculated at 45 kw/kg CN (20.4 kw/lb CN).

Little or no reduction occurred in metal concentrations, indicating that complexed metals remained in solution through the electrolytic process. This is probably influenced by the fact that "free" cyanide was always present in the discharge, presenting a ready source for complexing any metals that might otherwise have been removed from solution. It should also be noted that with the metals present (Fe, Zn, Ni and a minor amount of other heavy metals), no obvious effect on cyanide oxidation could be observed as a function of the concentration of these metals.

Analysis of the raw waste water shows that cyanate and ammonia are present. Cyanate (CNO^-) is formed by anode oxidation of CN^- in the plating bath, while low concentrations of NH_3 results from the slow hydrolysis of CNO^-. When comparing CNO^- concentrations in cell effluents with corresponding feed values, evidence is provided that the electrolytic process oxidizes CN^- all the way to CO_2 and N_2. With 65 percent oxidation of CN^- within the cell, for example, it would be expected that the CNO^- concentration would show a marked increase if this were the end product. Results show a CNO^- increase that is less than that calculated from CN loss. In some cases the discharge CNO^- concentration is less than in the raw waste. If the apparent loss of CNO^- is attributed to hydrolysis to NH_3, an appropriate increase in NH_3 would be noted. However, in 82 percent of the tests monitored (18/22) the NH_3 concentration in the discharge from the electrolytic cell was equal to or less than that entering the cell.

The drop in pH observed as the waste passes through the cell can be attributed to the formation of carbon dioxide (CO_2) which consumes alkali.

On several occasions during the demonstration period, oil entered the cyanide rinse system. It is believed that the oil came from cleaning baths and from the surface of the zinc plating solution. Excessive oil adsorbed on the carbon bed renders the latter ineffective for cyanide destruction and consequently leads to frequent bed replacement. If the degree of oil contamination is slight and infrequent, the bed will normally recover as the impurity is desorbed when oil-free rinse water is processed through the cells.

Chlorination Step -

Periodically the electrolytic process was by-passed to obtain operating data on chlorination of the raw waste for cost comparison purposes. The system installed provides for only high pH oxidation with hypochlorite. It must be realized that while the dominant reaction is one producing cyanate from the cyanide, some "chlorine" is consumed in oxidizing other species as well as a slight amount of cyanate, leading to slightly higher consumption rates.

The results obtained were good to excellent for cyanides amenable to chlorination and poor for the more refractory cyanide complexes. When the hypochlorite consumption was only slightly above the theoretical amount of 2.86 kg NaOCl/kg CN, marginal quality was obtained. At 50 percent excess, excellent quality was obtained. Higher hypochlorite feed rates did not improve oxidation of the more resistant cyanide complexes of nickel and iron.

In both the chemical and combined electrochemical/chemical treatment mode of operation, it was felt the additional hypochlorite consumption required to promote more consistently high removal rates was a proper manner to reduce pollution. With this in mind, the data that showed 4.5 - 5.0 kg NaOCl/kg CN are used for subsequent calculations.

Operating labor for the combined electrochemical-chlorination system amounts to 100 hr/yr and includes bed maintenance, hypochlorite handling and filter replacement. General maintenance labor requires 60 hr/yr, 40 percent of which was attributed to pump service. Operating labor for chemical treatment alone remained the same as with the combined electrochemical/chemical treatment. Additional labor in hypochlorite handling replaced bed maintenance labor. Maintenance labor decreased to 35 hr/yr with the elimination of the pump service requirements.

Batch Treatment

Spent process solutions containing high concentrations of cyanide (strip solutions, plating solutions, etc.) were isolated, stored and periodically oxidized by electrolysis in a batch process tank using conventional cell design. Dilute cyanide solutions (floor spills for the most part) were chlorinated in a batch mode using spent alkaline cleaners as a readily available source of alkali to maintain the desired high pH. Prolonged and detailed evaluations were not conducted as these processes are well described in the literature.

Electrolysis -

During the demonstration period several cell configurations were evaluated. Each varied slightly in anode to cathode spacing, electrode areas and anode material of construction. Variations in voltages required and current consumption were noted that could not be related to the amount of cyanide removed when comparing one series of tests to another. It is believed that these variations are more dependent upon cell configuration than upon any other fact. It is recognized that the resistivity to oxidation varies from one metal complex to the next and different results would be expected when comparing the treatment of nickel strip with a copper plating solution.

Removal rates varied from 68 g (0.15 lb) of CN per 1000 ampere-hours to 360 g (0.80 lb) per 1000 amp-hr. The curves shown in Figure 22 are typical in showing the change in concentration of total cyanide and amenable cyanides as a function of time. These tests were on 1150 l (300 gal.) batches at 96 - 102°C (205 - 215°F). The amenable cyanides were consistently oxidized (or converted to iron complexes) within three days. After that time, the rate of oxidation decreases drastically.

Chlorination -

Data consistent with information published on chemical consumption was obtained. With slight demands for hypochlorite the tendency to overtreat to save time was repeatedly demonstrated. It was felt that any attempt to use electrolysis in the semi-conductive bed technique for these collected dilute waste batches would prove futile due to the presence of oils from spent cleaners. Expenses known to occur with bed contamination exceeded any economic gain by electrolysis treatment.

NON-CYANIDE/CHROMIUM WASTE TREATMENT

A minor amount of studies were conducted on the waste waters normally considered free of cyanides and chromium compounds in order to obtain cost data to complete the total treatment system analysis.

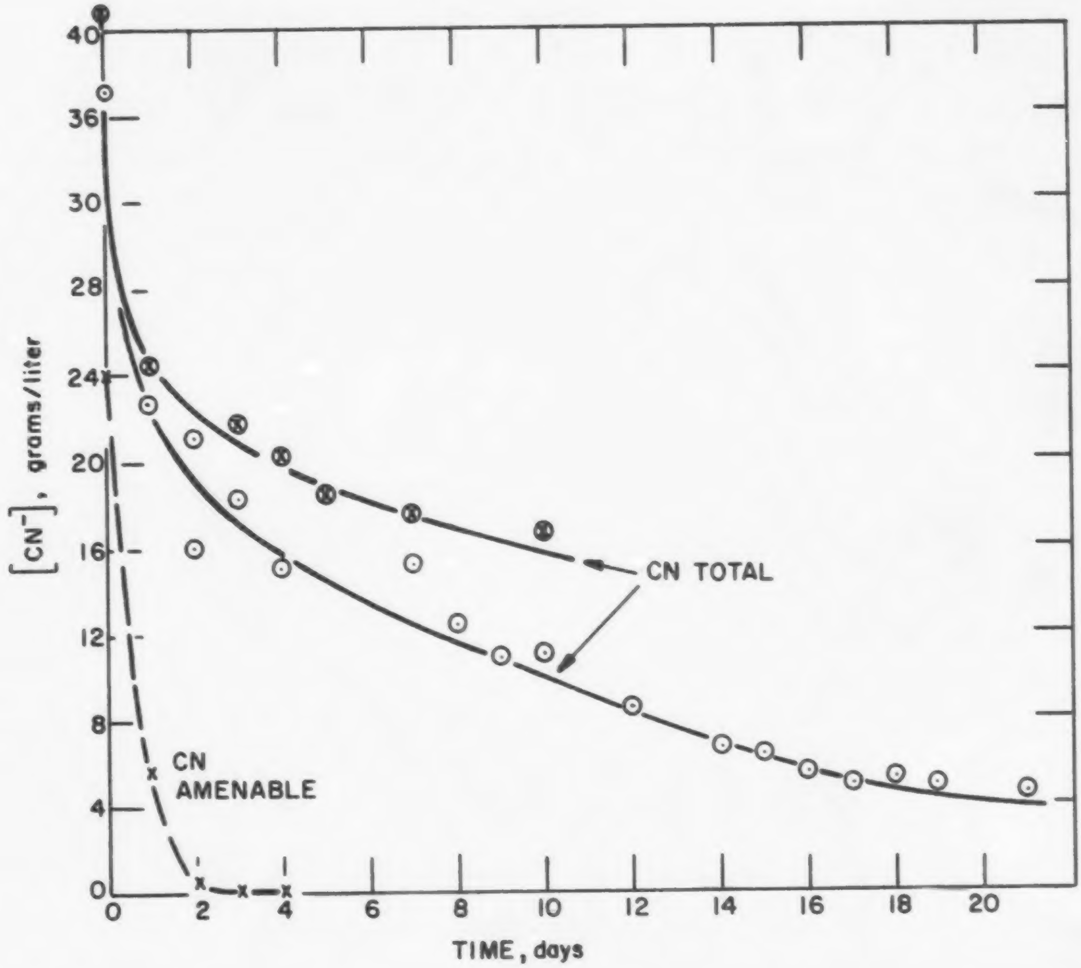


Figure 22. CN concentration during batch electrolysis

Characterization of Waste Water

Rinses known to be initially free of cyanides and chromium compounds were monitored. The original design criteria used a hydraulic loading of 225 l/min (60 GPM) and anticipated an acidic nature. Following water conservation-oriented changes and some process deletions, the flow averaged at 125 l/min (32.5 GPM) with occasional peaks of 325 l/min (85 GPM) as well as occasional periods of no flow. The pH monitoring of this raw waste showed a rather consistent range of 1.8 to 2.5.

Batch waste originally free of cyanide and chromium become intermixed with dilute cyanide batch waste water or dilute chromium batch waste water by the collection techniques employed. As a consequence, it is not possible to characterize the batches themselves. Since these waters are basically cleaners and pickles, their neutralization is simple and requires little if any discussion in this report.

Rinse Treatment

The neutralization sump receiving this raw waste water also receives the rinse water from the cyanide chlorination process. The collection system and the cyanide treatment system both operate in a pulsing mode. Consequently, there are periods when one or the other is not delivering waste to the sump. The cyanide waste is always alkaline and the non-cyanide rinse is always acidic. Therefore, this sump sees a wide range of pH values (1.8 to 12.0) in the raw waste.

The non-cyanide rinse water averages 125 l/min (32.5 GPM) and the cyanide treatment system contributes 75 l/min (20 GPM) for a total average flow of 200 l/min (52.5 GPM).

Operating labor amounts to 60 hr/yr for preparation of the dilute acid and alkali solutions used. Maintenance labor amounts to 20 hr/yr.

The pH is controlled at 7.0 to 8.5 with sulfuric acid and sodium hydroxide. Chemical consumption amounts to 8.2 kg (18 lb) per day of sulfuric acid and 34.5 kg (76 lb) per day of caustic soda.

SYSTEM ANALYSIS

There are three important areas in studying the results of the various systems. The combination of treated cyanide rinse water and neutralized rinses originally free of cyanide and chromium is of prime interest as this water is used for less demanding rinsing in the various metal finishing operations. Analysis of the total combined rinses leaving the treatment facility before solids removal indicates the quality of the treatment systems. The final discharge is of interest as it addresses the quality of the total plant.

Combined Rinses from Cyanide Treatment and from Those Initially Free of Cyanide and Chromium

Samples taken at various times throughout the day and over a two-week period were analyzed for the major contaminants that might influence the use of this second class water for rinsing. The range of cyanides amenable to chlorination was 0.11 - 0.55, with an average value of 0.23 mg/l. Hexavalent chromium was always below the limit of detection (0.00 mg/l). The pH ranged from 6.8 to 9.7 with an average value of 8.5. At an average volume of 200 l/min (52.5 GPM), this stream provides an ample supply of water with quality sufficient for rinsing after cleaning and pickling in the manner described in Section V.

Combined Rinses after Treatment

Filtered samples taken prior to solids removal were analyzed for cyanide and chromium. Cyanide amenable to chlorination was less than the design criteria of 0.1 mg/l. Average conditions showed less than 0.06 mg/l. Hexavalent chromium concentrations were also below the design criteria of 0.2 mg/l with averages less than 0.01 mg/l.

A typical analysis of a filtered sample is shown in Table 7.

In relating this discharge at 285 l/min (75 GPM) as a function of production in the same manner the initial pollution load was presented in Table 2, Section IV, one arrives at the data presented in Table 8.

Combined Rinses after Solids Removal

The results of the third important area, after solids removal, were not available at the time the project was completed. It was felt that the success in the re-use of partially treated water would eliminate the requirements for solids removal for water re-use. It was also realized that there will be little

Table 7. DISCHARGE AFTER TREATMENT

Cyanide, amenable	0.02 mg/l
Cyanide, total	8.3 "
Chromium, hexavalent	0.04 "
Chromium, trivalent	0.38 "
Copper	0.11 "
Zinc	0.5 "
Iron	0.8 "
Nickel	0.3 "
pH	8.4 "

Table 8. TREATED DISCHARGE AS A FUNCTION OF PRODUCTION

(on filtered sample)

	mg/m^2	$lb/10^6 ft^2$
Cyanide, amenable	1.61	0.33
Chromium, hexavalent	3.18	0.65
Chromium, trivalent	30.3	6.2
Copper	8.8	1.8
Zinc	40.1	8.2
Nickel	24.0	4.9
Iron	64.5	13.2
Dissolved solids	113,500	23,200
Suspended solids[a]	12,700	2,590

[a] prior to filtering

change in the concentration of dissolved materials as reported above. With less than 20 mg/l of suspended solids after settling, the total discharge would not change significantly for this plant. Consequently, the more important evaluations reported in Section VIII, Solids Handling, were given a higher priority.

SECTION VIII

SOLIDS HANDLING PROGRAM

GENERAL

Properly designed and operated waste treatment facilities produce effluents acceptable to regulatory agencies in that the discharge is considered safe for disposal to surface waters or to sanitary sewerage systems. In the process of chemically treating the waste water generated by metal finishing operations to render it non-toxic, solid waste is produced. The proper handling of these solids is essential to insure that any negative effect on the total environment is held to a minimum.

When considering the total impact on the environment caused by solids, one must address both the dissolved solids in the waste water and those solids that are not dissolved but are suspended and are carried along with the waste water. This section of the report is concerned only with those solids that are out of solution and is not concerned with the total dissolved solids content.

The treatment of metal finishing waste water normally consists of one or more processes used for oxidation of cyanide, reduction of hexavalent chromium, and pH adjustment. These processes may be either of batch operation or of continuous nature (or both). In the treatment of cyanide, the metals that had been in solution as the cyanide complex are removed from solution as the hydroxide.

Reduction of hexavalent chromium followed by pH adjustment produces insoluble trivalent chromium hydroxide. With the pH controlled to a value close to the minimum solubility of the various metal hydroxides, solids result that are suspended in the neutralized waste water. The combined waste streams normally contain objectionable amounts of these suspended solids.

Aside from the aesthetic appearance of waste water high in suspended solids, concern is expressed for the potentially toxic nature of these solids. In metal finishing waste, these solids contain a significantly high proportion of heavy metals. When discharged to a sanitary sewer, their accumulation in the sewage sludge presents problems. They may be toxic to the microorganisms in the sewage treatment plant. Their presence in the sewage sludge may prohibit use of the sewage sludge as fertilizer because of subsequent crop damage. If incineration is used for sewage sludge disposal, atmospheric pollution may result from the heavy metals present. When the metal finishing waste is discharged to surface waters, the solids will accumulate in the bottom of the streams or lakes. This silting action can significantly disturb the ecology of the organism originally living in this environment.

The need for removal of the precipitated solids has been well recognized. Low limits have been established for effluents discharge both to surface waters and to sanitary treatment systems.

Filtration of the treated waste water for solids removal is seldom considered because of the expense involved. The solids are relatively gelatinous in nature and rapidly restrict the flow of water through the filter. As a result, where space permits, the most commonly used approach for removal of suspended solids is through gravity settling.

The use of mechanical aids such as a series of parallel tubes across the top of the settling tank will significantly reduce the size of the equipment. An excellent discussion of this concept is provided by Lancy.[31]

Solids that have precipitated to the bottom of the settler must periodically be removed. Concentrations in the range of 0.5-2 percent solids are common to the metal finishing industry. The frequency of withdrawal and concentration is primarily dependent upon the detail design of the settler. This relatively low solids concentration requires further dewatering prior to ultimate disposal.

Thickening of sludge is an essential part of any solids handling program. Aside from the added cost of hauling water, there are other considerations requiring solids contents far higher than 0.5-2 percent. When used for land fill applications, the very "thin" sludge is impossible to contain within a given area, as the water will flow away, carrying solids with it. Compaction, common to most land fills, is impossible with excess water. A more desirable range is 15 percent (comparable to thick mud) to 35 percent (paste-like). Various techniques are available for thickening the sludge. The approach employed in this demonstration uses a centrifuge.

SOLIDS HANDLING AT NEW ENGLAND PLATING COMPANY

Characterization

The rinse waters contain suspended solids resulting from chromium and cyanide treatment processes and from acid/alkali neutralization. The average flow rate of the combined rinses is 284 liter/min (75 GPM). The suspended solids content is in the range of 100-225 mg/l.

Batch neutralization practices produce 24,000 liter/week (6350 gal./week) of waste water. Suspended solids contents seldom exceed 5 percent by weight. On two occasions higher values were obtained. Spent chromic acid anodizing solution and a spent chrome plating bath were treated, producing solids contents of 20-25 percent.

Facilities

A test settler was used to accelerate data collection after completion of the various tests described in the treatment study program. This unit is one-tenth the size of the production settler planned and has the same geometry as the full-sized settler. At the time of report preparation, the final production-size settler was still in the design stage. The test unit provided valuable information for this design. The data being reported is believed to be representative of that which will be experienced with the production-sized unit.

The information on sludge concentration was obtained from full-scale production equipment.

As an aid to understanding the solids handling facility, refer to Figure 23 for a schematic diagram of the installation. The combined rinse waters from the treatment area drain by gravity into a sump located in the Solids Handling Building. A pump is used to deliver the water to the tube settler.

Upon entering the settler, the waste water passes through a chamber to permit the formation of flocculant particles. After flocculation the water enters the settling chamber, flowing in an upward direction, through the tubes and overflowing at the top by way of an overflow dam. The clarified water drains by gravity into an observation sump and finally to a sewer leaving the plant.

The suspended solids precipitate in the settling chamber, flowing counter-current to the water itself. The solids drop to the bottom of the settling chamber and slowly accumulate. Periodically the accumulated solids are withdrawn from the bottom of the settling tank.

A centrifuge is used for concentration of the sludge. The solids withdrawn from the bottom of the settling tank are pumped into the centrifuge. Centrate leaving the centrifuge

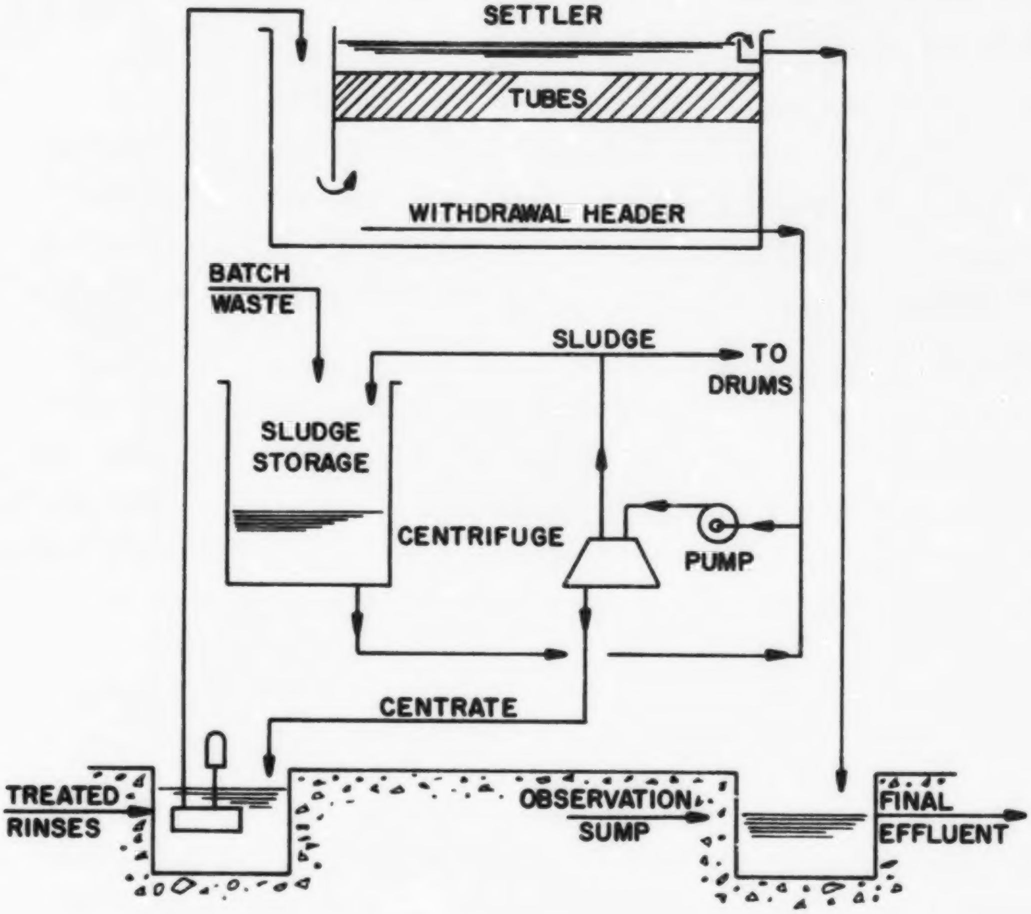

SETTLER
TUBES
WITHDRAWAL HEADER
BATCH WASTE
SLUDGE
TO DRUMS
SLUDGE STORAGE
CENTRIFUGE
PUMP
CENTRATE
TREATED RINSES
OBSERVATION SUMP
FINAL EFFLUENT

Figure 23. Solids handling schematic

drains by gravity into the sump receiving the combined rinse from the treatment area, and passes through the settling operation a second time.

The partially concentrated sludge is delivered to a sludge storage tank whenever the sludge leaving the centrifuge is below 15 percent solids.

The partially thickened sludge is periodically withdrawn from the sludge storage tank for another pass through the centrifuge. With a higher feed concentration, the centrifuge produces the thick sludge desired (15-30 percent). The centrate during this operation is again recycled through the settling tank.

Waste water produced by batch treatment practices is normally higher in solids content than the rinse waters. These wastes are transferred from the batch treatment tanks directly to the sludge storage tank and are processed along with partially thickened sludge.

The thickened sludge is placed in drums for hauling away to a suitable land fill operation.

DEMONSTRATIONS

Suspended Solids Removal

In operating the test tube settler, a portion of the total waste water was used under varying hydraulic loadings. Measurements of suspended solids were made on both the feed water and the settler effluent. To study various hydraulic loading effects (and a corresponding total solids loading), the unit was run for several days at any given flow rate to establish what was considered equilibrium conditions between solids entering and solids leaving.

The range of flow rates used was 22.7 to 56.7 liter/min (6 to 15 GPM). This corresponded to a range of velocities through the tubes of 0.05 to 0.13 cm/sec. (0.1 to 0.25 ft/min).

The data obtained are shown in Figure 24. The results show the optimum flow rate to be near 37.8 liter/min (10 GPM) when considering the quality of effluent. Lower flow rates did not improve the quality. It will be noted that when the solids concentration into the settler at the low flow rate rose to four to five times the average concentration at New England Plating, the quality of discharge improved significantly and approached that of the more ideal flow rate. This fact may indicate that equilibrium conditions had not been reached at the lower concentrations for this low flow rate.

As would be expected, the quality of effluent suffered when a high flow rate was used. The shorter contact time in the unit, together with the higher velocities in the tubes, permitted excess solids to escape in the effluent.

The frequency of removal of suspended solids in this test settler was observed under various operating conditions. If the period between removal was too long, the quality of effluent suffered. In addition, when the solids became too

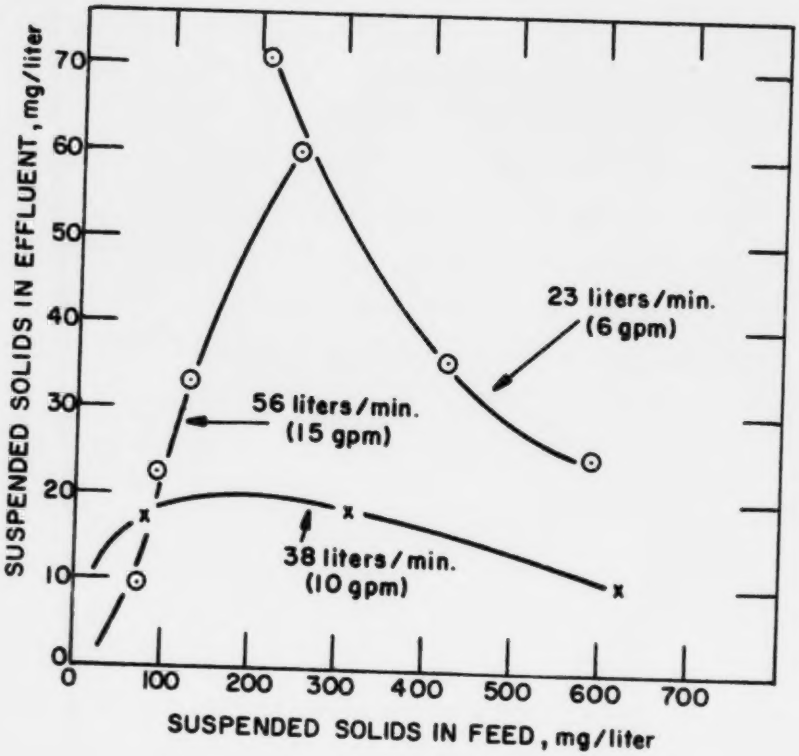


Figure 24. Settler effluent under solids input variations

concentrated after too long a period between withdrawal, the sludge header in the bottom became blocked with solids. Since the primary concern was the removal of suspended solids from the waste water, and not with the design of the bottom of the tube settler, little factual data can be presented.

Sludge Concentration

The centrifuge employed in this demonstration was obtained from Leon J. Barrett Company. This unit employs a continuous-intermittent cycle. Waste is introduced into the bowl for a preset time. The unit then continues to spin for a second preset period. Finally a scoop removes the accumulated sludge from the bowl, completing the cycle. The feed rate becomes a fourth variable. The unit used has a maximum hydraulic loading of 37.8 liter/min (10 GPM).

At a given hydraulic loading, the time of the feed determines the total solids loading, and is perhaps the most significant variable. During the feed period, the amount of solids removed decreases as the sludge accumulates. With this centrifuge design, any excess of solids that cannot be retained within the unit escapes into the centrate.

During the demonstration period, little effect was noticed by variations in the length of the second step during which the accumulated sludge in the bowl is dewatered. Variations in the time required to removed the accumulated and dewatered sludge from the bowl also did not produce any significant results in the concentration of sludge discharged.

During the evaluations, various concentrations of solids in the feed to the centrifuge were processed. At a given hydraulic loading, the other three machine variables were adjusted to produce what was considered to be the optimum conditions for producing the most dense sludge. Comparison of the sludge density before and after the centrifuge showed the concentrating effect obtained. In feed ranges of 0.7 - 1.6 percent at 37.8 liters/min (10 GPM), the solids content increased an average of 19 times (i.e., a feed at 0.71 percent resulted in a sludge at 13.5 percent solids). When the hydraulic loading was changed to 18.9 liters/min (5 GPM), this same comparison showed the solids content increase to average 20 times the feed concentration.

During this same period, measurements of solids content in the centrate were made to determine the percent of solids in the feed that were captured by the centrifuge. The controlling factor was demonstrated to be the hydraulic feed. At the lower hydraulic loading, 50 percent of the solids in the feed were captured; at the higher value, the average amount captured was only ten percent of the feed solids. When the hydraulic loading was kept at the lower volume and the duration of feed into the centrifuge was reduced, the percent of solids captured increased to 56 - 63 percent as the feed time per cycle was steadily decreased. At the lower feed time, the solids content in the sludge discharge decreased.

DISCUSSION

The rectangular tubes used in this demonstration were obtained from Neptune Microfloc Company. Other shapes are available and may well produce results that vary from those demonstrated.

All data presented on the settler were obtained without the use of coagulant or polyelectrolyte addition agents. It is felt that the proper application of these chemicals will further enhance solids removal, especially for the smaller particles approaching colloidal size.

Time did not permit evaluations of these two factors during the demonstration period. As a result, the 37.8 liters/min (10 GPM) flow rate has been selected for final settler design. It is felt that further investigations will result in further improvements. However, the effluent discharge meets the current regulatory requirements.

The design of the sludge accumulation section in the bottom of the tube settler determines the degree of concentration obtainable. Important factors to be considered in this design include the frequency of solids withdrawal, the amount removed at any given time, and, of course, the physical technique employed for withdrawal. From preliminary observations, it is felt that the sludge accumulation section in the production unit will be larger than that used in the test unit. In this manner, there will be a smaller impact of the effluent quality as the sludge accumulates.

With the centrifuge being used for sludge concentration, the centrate is intermixed with the treated water and passed through the settler for another pass. This recycle of solids increases the settler feed concentration for levels considerably higher than the normal rinse waters. Values as high as 1300 mg/l were witnessed. Except when the hydraulic loading exceeded 38.4 l/min (10 GPM), the settler effluent quality improved at higher feed concentrations. With the feed at a level of 600 to 675 mg/l, effluents in the 10-12 mg/l range were obtained. In the test at 1300 mg/l, the effluent was 1 mg/l. These observations appear to support the advantages of sludge recycling. Taylor and Jester[32] describe their success in sludge recycling at a brass mill treatment plant. It is believed future developments in this concept will enhance tube settler performance.

It is recommended to others considering the tube settler approach to removal of suspended solids that they use a pilot operation on the actual waste to maximize the advantages of the tube settlers in reducing capital and space requirements.

For efficient centrifuge operation, the initial consideration should be the hydraulic loading. As shown, lower feed rates show significant improvement in the amount of solids captured by the centrifuge. With higher capture, it is believed a greater concentrating effect can also be achieved. Caution must be observed that the feed concentration is not too high as the mechanism employed for removing the sludge from the centrifuge used in the demonstration becomes plugged by the very dense sludge. It is believed that with the variables available in operating the machine, a wide range of feed concentration can be properly handled. At low concentrations, multiple passes will result in the dense sludge desired for land disposal. Since the centrate contains significant solids concentration (even at 80 percent capture), it is required that this waste water be returned to the settler for recycle. Fortunately, settler studies show an improved effluent quality with higher feed concentrations.

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32. Taylor, T. H., and T. L. Jester. Industrial Waste Treatment at Scovill Manufacturing Co., Waterbury, Connecticut. (presented at the 28th Purdue Industrial Waste Conference. LaFayette, Indiana. May 2, 1973.) 16 p.

SECTION IX

DISCUSSION

GENERAL

This section of the report provides a summary discussion of the in-plant changes prompted by waste treatment practices, the effectiveness and efficiencies of the chromium and cyanide systems, as well as a cost analysis of each, and of the total treatment plant. In addition, guidance for others is provided and a brief description of parallel electrolytic treatment work done concurrently with this demonstration project.

IN-PLANT CHANGES

In resolving the pollution problems initially presented, many in-plant changes were prompted that not only affected the waste treatment facility, but also the processing of parts being plated.

Previously there were a variety of cleaning and pickling processes available to accommodate all the needs of many and varied customers. In order to reduce the complexity of the pretreatment processing, these processes were reduced in number and those selected would successfully prepare the greatest amount of production. In a few cases when customer's work would not be satisfied by the resulting processes, the work was refused.

Processing of aluminum alloys was never considered a significant volume in respect to total plant production. Rather than install isolation and collection piping, the work was discontinued and process equipment removed. Process operations deleted included sulfuric acid anodizing and dyeing, chromic acid anodizing, hard coating of aluminum and conversion coating application. For the same reason, phosphating of steel was discontinued.

As explained earlier, the water conservation practices started earlier were accelerated to reduce the hydraulic loading on the treatment facility. Initially the plant was separated into process centers for cost control purposes. Each process center was supplied with its own water distribution system. Past practices had been to hold the machine operator (or process center lead operator) responsible for production and quality at his process center. The operator's job description was expanded to include concern for water conservation. The extended counterflow rinse systems reduced the amount of involvement for the operator, as well as water consumption.

In addressing the optimum rinse water flow, flow rates were selected after a variety of tests at higher and lower flows. A minimum flow was determined that was consistent with quality objectives and solution life. A slightly higher value was used to provide a safety margin. In some cases, reductions of better than 70 percent were realized. In the overall plant, attention to water conservation reduced the hydraulic load by better than 30 percent in the raw waste. This reduction in the amount of water purchased by New England Plating Company resulted in a savings of $2867 per year.

The program for re-use of treated water is continually being expanded after a thorough investigation at each location. At the time of writing this report, this second class water is being effectively used following cleaning and pickling steps, as well as for maintenance cleaning. It is expected that this program when fully implemented will reduce the amount of plant discharge by an additional 15 percent through re-use of 30-35 percent of the treated water.

Additional attention is being given to solution life. With the added cost of batch treatment, there is a greater economic incentive to longer use of process solutions than before pollution control went into effect.

During the demonstration program, more automatic processing equipment was installed with a corresponding decrease in hand processing. While the major reasons for the change to automation were based upon normal business considerations, waste treatment considerations did have an effect. In hand operations, additional counterflow rinsing increases labor costs. The chance of operator error in using the wrong rinse tank is eliminated with automation. When a given hand operated process center was replaced by automatic machines, the high cost associated with isolation of drain lines with the replaced hand line was avoided and influenced financial considerations.

CHROMIUM TREATMENT

In discussing the effectiveness and efficiencies of the chromium treatment system at New England Plating, it must be recognized that the electrochemical process and the equipment employed should be separate and distinct subjects. The equipment installed was sized to treat 120 mg/l of hexavalent chromium with an anticipated cell discharge of less than 0.2 mg/l. During the demonstration period, the average concentration of hexavalent chromium in the normal rinse waters was 17 mg/l. As a result, the length of travel through the cells was greater than required for this concentration. It is believed that this is the single most important factor contributing to the superior treatment achieved. With only 15 percent of the anticipated hexavalent loading, it is understandable as to why the discharge was an order of magnitude lower than anticipated. At higher feed concentrations (100-150 mg/l) the cell discharge was closer to the predicted value.

Control of the pH of raw waste entering the electrolytic cells is essential for maintenance of the electrochemical reduction process. At concentrations of hexavalent chromium less than 50 mg/l, a pH of 1.8-2.1 is adequate. As the concentration is increased to values as high as 150 mg/l, lower pH values in the range of 1.5 to 1.6 are preferred.

With the electrolytic process, the amount of chromium reduced is dependent upon pH, concentration of hexavalent chromium and distance of travel through the bed at a given velocity. Most of the data was obtained in the narrow pH range of 1.8-2.1. From the limited data available, it is believed that lower pH values will result in greater reduction rates. If the extent of reduction (mg/l reduced per meter of travel) is plotted against the initial hexavalent chromium concentration, a curve as shown in Figure 25 is obtained.

The limited experiments directed towards removal rate variations with applied power variations indicated that after a threshold voltage is reached, no significant improvement is obtained with higher voltages. From a process standpoint, the voltage depends upon the spacing between major electrodes. The distance in these specific cells is 15 cm (6 in.). With a greater distance, it is expected that a higher voltage would be required. The demonstration cells under normal operating conditions used 7.5 v. When higher chromium concentrations were being processed, this minimum voltage was 8.0 v.

In considering the efficiency and effectiveness of the electrolytic process itself, it is believed that a very stable process exists that should be considered for other applications. Initial results can be misleading because the adsorption effect will show extremely high removal rates. However, after this initial period, a steady state will exist for reduction of hexavalent chromium.

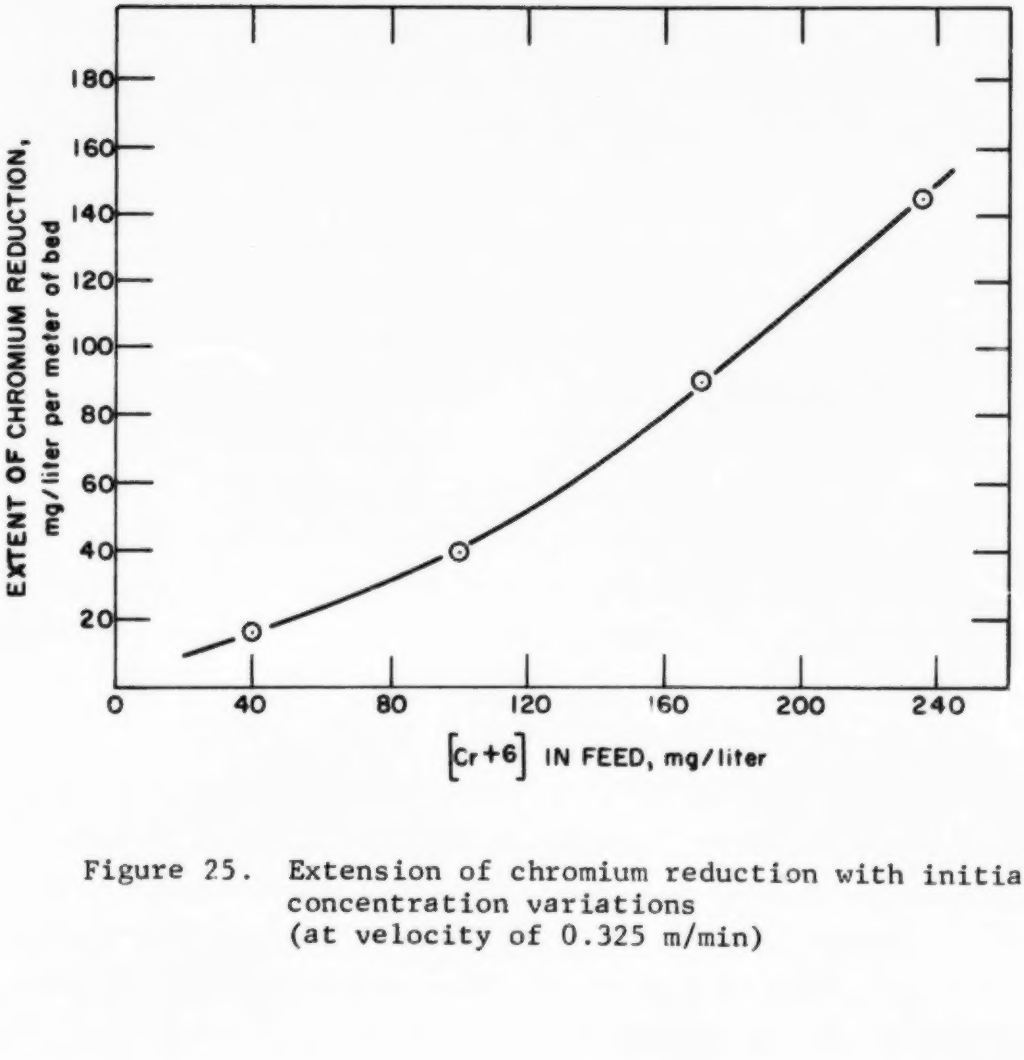

Figure 25. Extension of chromium reduction with initial concentration variations (at velocity of 0.325 m/min)

In order to consistently maintain a low level of discharge, it is important to use a contact time adequate for the highest feed concentration and not the average concentration.

Power consumption varies with the chromium concentration in the waste being treated. For a 75 l/min (20 GPM) flow at 17 mg/l, 1.4 kw of power was consumed. At the same flow rate but at 156 mg/l, 2.0 kw of power was used. This results in these cells reducing nine times the amount of chromium with only a 40 percent increase in power. Figure 26 shows the results obtained during the demonstration for the amount of chromium reduced per kilowatt hour as a function of hexavalent chromium loading.

The pH adjustment step following the electrolytic reduction process proved effective in trivalent chromium hydroxide formation. The performance was considered typical for comparable processes employed in this industry.

Equipment Costs

The equipment costs provided in Table 9 represent purchase prices to New England Plating factored for an average flow rate of 75 l/min (20 GPM). It should be recognized that this equipment was purchased and installed in 1971. Price adjustment undoubtedly would influence the capital picture today, whether caused by inflation or by advances in cell construction technology.

It is estimated that equipment that would normally be selected for bisulfite reduction if used in place of the electrochemical process would cost the amount shown in Table 10.

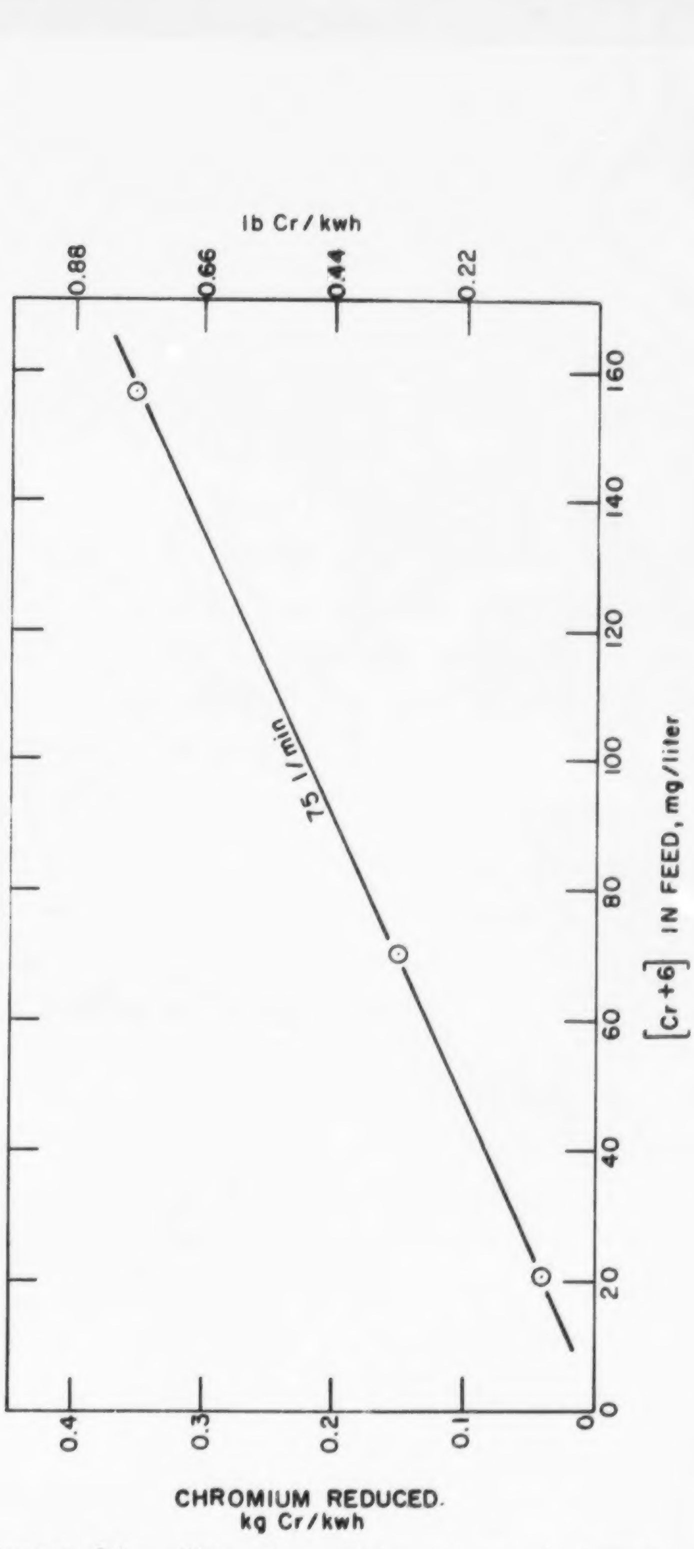

Figure 26. Chromium reduced per kilowatt hour vs hexavalent chromium concentration

Table 9. ELECTROCHEMICAL REDUCTION SYSTEM EQUIPMENT COSTS

pH control system (raw waste)	$ 1,400
Surge tank	1,825
Transfer pump	965
Filters (2)	310
Electrochemical cells (2)	18,900
Rectifier	450
pH control system (reduced waste)	2,100
Electrical controls	225
Total Equipment	$26,175
Installation costs	
(rigging, plumbing, electrical)	
electrochemical system	$ 3,800
precipitation system	1,075
Total installation cost	$ 4,875
Total installed cost	$30,050

Table 10. CHEMICAL REDUCTION SYSTEM EQUIPMENT COSTS

Reduction tank	$ 1,900
pH control system (reduction step)	1,400
ORP control system	1,400
Agitator	1,000
pH control system (reduced waste)	2,100
Electrical controls	225
Total equipment	$ 8,025
Installation costs	
(rigging, plumbing, electrical)	
reduction step	$ 1,075
precipitation step	1,075
Total installation cost	$ 2,150
Total installed cost	$10,175

Operating Costs

Operating costs are provided for both the electrochemical (Table 11) and the chemical (Table 12) reduction processes. Figures are provided at two chromium concentrations in the raw waste. Data given are on an annual basis with 16 hr/day of production (4000 hr/yr) for a 75 l/min (20 GPM) flow.

Operating costs shown for the chemical reduction step on dilute waste were obtained from operating history. Figures shown for the high chromium level are calculated by adding the theoretical amount required to lower the chromium level to the lower point of the operating data for the lower level.

Cost Comparison

Direct comparison between the two operating modes shows that at the low concentrations of hexavalent chromium, there is no significant operating cost advantage of one system over the other. However, at higher concentrations, the economic advantage of the electrochemical process would pay for the additional capital investment in four to five years.

At New England Plating, treatment of 450 kg (1000 lb) of chromic acid from spent chromate solutions in the rinse water system will permit greater utilization of the electrochemical system and avoid chemical costs and labor associated with batch reduction.

Other Considerations

In drawing too significant a cost comparison, one must remember that the New England region has higher than national

Table 11. OPERATING COSTS FOR ELECTROCHEMICAL REDUCTION & PRECIPITATION

(annual basis)

Item	$[Cr^{+6}]$ at 17 mg/1		$[Cr^{+6}]$ at 156 mg/1	
	amount	cost	amount	cost
Sulfuric acid	3340 kg (7350 lb)	$ 440	3340 kg (7350 lb)	$ 440
Carbon bed replacement	218 kg (480 lb)	480	241 kg (530 lb)[a]	530
Sodium hydroxide	3720 kg (8200 lb)	1560	9530 kg (21,000 lb)[a]	4000
Sodium hydrosulfite	7 kg (15 lb)	15	7 kg (15 lb)	15
Electricity, cell use	5500 kwh	175	8000 kwh	254
Electricity, other use	14,700 kwh	468	14,700 kwh	468
Replacement parts				
anodes for cells		640		765[a]
filter cartridges		297		297
miscellaneous		246		246
Labor				
operating, reduction step	100 hr	350	100 hr	350
operating, precipitation step	100 hr	350	200 hr[a]	700
maintenance, reduction step	70 hr	280	70 hr	280
maintenance, precipitation step	25 hr	100	25 hr	100
Total direct cost to operate		$5401		$8445

At 75 l/min (20 GPM) $17.20/kg Cr ($7.82/1g) $2.94/kg Cr ($1.33/1b)

[a] Estimates

Table 12. OPERATING COSTS FOR CHEMICAL REDUCTION AND PRECIPITATION

(annual basis)

Item	$[\mathrm{Cr}^{+6}]$ at 17 mg/1		$[\mathrm{Cr}^{+6}]$ at 156 mg/1	
	amount	cost	amount	cost
Sulfuric acid	2870 kg (6325 lb)	$ 380	10,200 kg (22,500 lb)	$ 1350
Sodium bisulfite, anhydrous	1850 kg (4075 lb)	895	8800 kg (19,400 lb)	4270
Sodium hydroxide	3720 kg (8200 lb)	1560	9530 kg (21,000 lb)	4000
Electricity	18,500 kwh	588	18,500 kwh	588
Replacement parts		196		196
Labor,				
operating, reduction step	170 hr	595	450 hr	1575
operating, precipitation step	100 hr	350	200 hr	700
maintenance, reduction step	50 hr	200	50 hr	200
maintenance, precipitation step	25 hr	100	25 hr	100
Total direct cost to operate		$4864		$12,979
At 75 1/min (20 GPM)	$15.50/kg Cr ($7.05/lb)		$4.50/kg Cr ($2.05/lb)	

averages for power costs. It should also be considered that the power costs shown represent prices that reflect upon the "fuel crisis" under which the utilities had been permitted to increase their rates to consumers. The prices shown for chemicals represent prices that had only recently been released from Federal price control and do not necessarily reflect upon the anticipated price increases expected by economists.

An advantage of the electrochemical treatment system that may readily be overlooked is the impact upon the total dissolved solids in any given installation. The use of derivatives of SO_2, or for that matter other reducing chemicals, introduces additional dissolved solids to the waste water. The bisulfite used in the demonstration increased the sulfate concentration in the final effluent. When the electrolytic process is employed, less sulfate is discharged to the environment.

CYANIDE TREATMENT

In discussing the effectiveness and efficiencies of the cyanide treatment system at this installation, it is also important (as with chromium treatment) to consider the electrochemical process separate from the specific equipment employed.

The equipment installed was sized to treat 30 mg/l. With an anticipated efficiency of 90 - 95 percent, the cells would have discharged less than 2 mg/l. During the demonstration period the average concentration of cyanides amenable to chlorination was 80 mg/l. The average concentration of total cyanides was 110 mg/1. The average removal was 52 mg/1. While more cyanide was removed electrolytically than had been anticipated, these cells had an overall removal efficiency of 65 percent when 40 volts was applied.

These cells have an effective length of solution contact that is 2.5 m (100 in.). Samples withdrawn at intermediate points along this contact route show a straight line relationship for removal of cyanide (except at very low concentrations). At 20 percent of the distance of travel (0.5 m), 20 percent of the cyanide being removed was removed. At 60 percent of the distance, 60 percent was removed. Based upon these observations, it is believed that 20 mg/1 is being removed for each meter of travel (0.5 mg/1 per in.). Had cells been selected that had a length of travel of four meters, the average discharge from the cells would have been closer to the design concept of 2 mg/1. The distance between major electrodes in these cells is 15 cm (6 in.). Previous work with other cyanide solutions had indicated a potential between these electrodes 12-14 volts would be adequate. However, the work done during the demonstration shows that with cyanide rinses that are predominately from zinc plating, higher potentials are required.

In considering the efficiency and effectiveness of the process itself and taking into account the cell design considerations just covered, it is believed that a stable process exists. Initial results can be misleading because the adsorption effect will show extremely high removal rates.

However, after this initial period, a steady state will exist for removal of cyanide.

In order to consistently maintain a low level of discharge, it is important to use a contact time adequate for the highest feed concentration. At this facility, with concentrations at 140 mg/l for 10 percent of the time, it is believed that a bed length of 7-8 meters would be required. This would be roughly twice the size of that required for the average concentration in the feed. The equipment costs for maximum loading would be higher than for average loading. If this route is selected, then the process will exhibit an even greater stability since the last portion of the bed will normally only receive very low concentrations and the adsorption role would probably play a dominant role for a long period of time.

When this demonstration project was initiated, power costs were approximately one-third of that existing at the end of the project. Initial considerations showed a significant cost advantage in using the electrolytic process over the chlorination process. During the investigation it was established that the amount of power required was two to three times that expected. This discovery, together with the increased power costs, resulted in an economic picture significantly different than that initially predicted. In reviewing the removal rate variations, demonstrated to be affected by applied voltage, one can establish an optimum trade-off between power costs for electrochemical removal rates and hypochlorite costs. During the demonstration, 40 v. was used. A slightly lower value would have been more economical. Hypochlorite was in short supply and price increases were anticipated. For this reason, the higher voltage was selected to establish data over a long period.

The chlorination system installed following the electrochemical treatment step proved effective when adequate excess hypochlorite was maintained.

For the total cyanide system, effective and efficient treatment of cyanides amenable to chlorination was achieved. Normally one would expect those cyanides represented by the difference between total cyanide and amenable cyanides to show an inferior removal rate. In the average conditions during the demonstration this difference is 30 mg/l (CN_t @ 110 mg/l and CN_a @ 80 mg/l) in the raw waste. These more refractory cyanides were partially removed. While the total system, i.e., electrochemical/chlorination, removed more of these tightly complexed cyanides than anticipated, time did not permit thorough studies of the treatment of iron and nickel cyanide complexes.

Equipment Costs

The equipment costs provided in Table 13 represent purchased prices to New England Plating factored for an average flow rate of 75 l/min (20 GPM). It should be recognized that this equipment was purchased and installed in 1971. Price adjustments undoubtedly would influence the capital picture today, whether they be caused by inflation or by advances in cell construction technology.

Table 13. ELECTROCHEMICAL & CHEMICAL TREATMENT EQUIPMENT COSTS FOR CYANIDE REMOVAL

Surge tank	$ 1,500
Transfer pump	965
Filters (2)	310
Electrochemical cells (2)	18,900
Rectifier	1,500
Chlorination equipment	3,200
Electrical controls	225
Total equipment	$26,600
Installation costs (rigging, plumbing, electrical)	
electrochemical system	$ 3,600
chlorination	1,175
Total installation costs	$ 4,775
Total installed cost	$31,175

Operating Costs

Operating costs are provided for both the electrochemical/chemical operating mode and the chlorination mode alone (Tables 14 and 15, respectively). Figures given are on an annual basis with 16 hr/day of production (4000 hr/yr) for a 75 l/min (20 GPM) flow.

Cost Comparison

Direct comparison between the two operating modes shows a cost reduction of $1,855 per year with electrolysis in use. However, it must be remembered that the electrochemical system shows evidence of complete oxidation to carbon dioxide and nitrogen, while the chemical oxidation step employed is known to only oxidize cyanide to cyanate. Had the two-step chlorination process been employed to oxidize the cyanide to carbon dioxide and nitrogen, the direct costs have been calculated to increase by $16,675 for chemical oxidation and $7,185 for the electrochemical/chemical mode. Under these circumstances, the cost advantage of the electrolytic process increases to approximately $11,000 per year.

Other Considerations

In drawing cost comparisons, one must remember that New England has a higher than national average cost for electricity. It must also be remembered that the power costs shown represent prices that reflect upon the "fuel crisis" under which the utilities had been permitted to increase their rates to consumers. The prices shown for chemicals represent prices

Table 14. OPERATING COSTS

FOR ELECTROCHEMICAL/CHEMICAL OXIDATION

(at 65% by electrolysis, 35% by chlorination
on annual basis)

Item	Amount used	Cost
Sodium hypochlorite	27,000 l (7200 gal.)	$3600
Carbon bed replacement	218 kg (480 lb)	480
Electricity, cell use	60,000 kwh	1910
Electricity, other use	10,000 kwh	320
Replacement parts,		
anodes for cell		240
filter cartridges		400
miscellaneous		130
Labor,		
operating	100 hr	350
maintenance	60 hr	240
Total direct cost to operate		$7670

At average conditions of 102 mg/l CN removed from a 75 l/min (20 GPM) flow:

$4.14/kg CN or $1.83/lb CN

Table 15. OPERATING COSTS FOR CHEMICAL OXIDATION

(annual basis)

Item	Amount	Cost
Sodium hypochlorite	66,000 l (17,600 gal.)	\$8800
Electricity	5500 kwh	175
Replacement parts		60
Labor,		
operating	100 hr	350
maintenance	35 hr	140
Total direct cost to operate		\$9525

At average conditions of 102 mg/l CN removed from a 75 l/min (20 GPM) flow:

\$5.14/kg CN or \$2.33/lb CN

that had only recently been released from Federal price control and do not necessarily reflect upon the price increases expected.

One advantage of the electrochemical treatment process not covered earlier is concerned with the impact of this system on the total dissolved solids content. By replacing chlorination with electrolytic treatment, a significant reduction in chloride can be expected in the final effluent.

TOTAL WASTE TREATMENT PLANT

In discussing the overall effectiveness of the waste treatment plant prior to solids removal, comments are being offered on analytical data coming from filtered samples so as to remove from any issues those contaminants that might remain after solids removal. In this manner, the electrochemical and chemical treatment systems themselves may be properly discussed.

A comparison of the initial raw water contamination level prior to the installation of the waste abatement system and the final discharge during the study period, as well as the relationships to production, is provided in Table 16. Analysis of this data shows the superior results of the treatment facility. For cyanides amenable to chlorination and hexavalent chromium effluent analysis consistently is lower than the originally anticipated effluent. For cyanides not amenable to chlorination, higher than desired values are seen. However, it is believed the low quantity (8.3 mg/l)

Table 16. MAJOR CONTAMINANTS BEFORE AND AFTER TREATMENT

	Before at 757 l/min (200 GPM)			After at 274 l/min (75 GPM)		
	mg/l	mg/m^2[a]	lb/10^{6}ft^2[a]	mg/l	mg/m^2[a]	lb/10^{6}ft^2[a]
Cyanides, amenable	4	920	188	0.02	1.61	0.33
Cyanides, total	NA	-	-	8.3	660	135
Chromium, hexavalent	24	5,500	1,125	0.04	3.18	0.65
Chromium, trivalent	11	2,520	516	0.38	30.3	6.2
Copper	0.5	112	23	0.11	8.8	1.8
Zinc	0.2	44	9	0.5	40.1	8.2
Nickel	4	900	188	0.3	24.0	4.9
Iron	2	460	94	0.8	64.5	13.2
Solids, total dissolved	1036	238,000	48,600	1422	113,500	23,200
Solids, suspended[b]	46	10,500	2,160	159	12,700	2,590

[a] related to production volume

[b] prior to filtration

Note: With suspended solids removal to 20 mg/l, contamination of fully treated effluent as related to production volume becomes 1,597 mg/m^2 or 326 lb/10^{6}ft^2.

will have little effect upon the environment. Any attempt to lower this material must rest with reduction of quantity at the source, namely in the zinc and copper plating solutions themselves. The treatment facility will do no more than is presently being done.

In regard to the total dissolved solids, the concentration in the discharge has increased. With the reduction in volume that has taken place, there is better than a 50 percent reduction in the TDS when the total environment is considered. It should also be recognized that of the TDS, at least 37 percent comes from the waste treatment chemicals themselves, and not from the production facility.

The sludges generated by the waste treatment processes will ultimately be hauled away by a State licensed contractor for disposal in an appropriate landfill. The metal hydroxides in the sludge will not pose a threat to the environment when handled in this manner.

Of the products produced by the treatment facility, only the treated water is considered recoverable. The various metal hydroxides are intermixed and of little interest for salvage due to the low volume and high expense of separation. Only partial recovery of water is anticipated. The high dissolved solids content in the treated water limits its use in the production facility.

Capital Costs for Total Plant

Those items normally considered to be capitalized are summarized in Table 17.

Table 17. CAPITAL COSTS FOR TOTAL PLANT

System	Equipment	Installation
Isolation and collection	$ 13,312	$25,900
Cyanide rinses	26,600	4,775
Chromium rinses	26,175	4,875
Non-CN/Cr rinses	2,700	1,325
Batch	11,348	4,300
Solids handling	29,790	7,150
Miscellaneous	1,500	300
Total	$111,425	$48,625

Total equipment	$111,425
Total installation	48,625
Waste treatment building	23,047
Engineering fees	18,000
Total capital cost	$201,097

Operating Expense for Total Plant

The annual operating expense for the waste treatment facility is shown in Table 18. The costs shown for the solids handling are those projected and are based upon the data obtained from pilot runs.

Waste Treatment Costs Relative to Production

Waste treatment costs discussed earlier have been provided as an aid to others designing and selecting specific types

Table 18. DIRECT OPERATING EXPENSE FOR TOTAL TREATMENT PLANT

(per year)

System	chemicals	electricity	parts	labor-oper.	labor-main.	total
Chromium rinse	$ 2,495	$ 643	$1,183	$ 700	$ 380	$ 5,401
Cyanide rinse	4,080	2,230	770	350	240	7,670
Non-Cr/CN rinse	389	162	50	210	80	891
Batch	4,935	1,700	125	1,138	225	8,123
Solids handling*	250	225	150	1,400	225	2,250
Total	$12,149	$4,960	$2,278	$3,798	$1,150	$24,335

*estimated

of treatment. It is also believed that the total expenses incurred at this facility should be related to production volume. In a captive shop, it is easy to relate the waste treatment expenses to the specific items being manufactured. In a diversified job shop, serving many different customers with a wide variety of parts, the only suitable relationship can be to one that is relative to added value, or dollar volume of production. A summary of waste treatment costs on an annual basis is given in Table 19.

Table 19. SUMMARY OF WASTE TREATMENT COSTS

(annual basis)

Labor	$ 4,948
Purchases	19,387
Applied overhead	9,401
Capital depreciation*	36,532
Total annual cost	$70,268

*depreciation of non-building capital is 5-year, straight line and for building capital, 25-year, straight line.

This value is considered total annual expense. Since a portion of the treated water is essentially reclaimed water, a net operating expense is obtained by deducting from the total annual expense, the value of re-used treated water. At New England Plating, it is projected that 30-35 percent of the treated water will be re-used, with a savings of 22.6×10^6

l/yr (6.0 x 10^6 gal./yr). At the present cost of water in Worcester, Massachusetts, a salvage value of $1600 is anticipated. This will result in a net annual expense of $68,668.

Based upon current business dollar volume, the total cost of waste treatment represents 6.4 percent of sales and the net cost is 6.25 percent of sales.

PARALLEL WORK WITH ELECTROLYSIS

During the demonstration project, there were considerable hardware and process developments, as well as several other applications using the same basic semi-conductive bed electrochemical technology. A brief description of the more significant aspects of this parallel work is being offered as additional information. These details relate to cell design, applications within the Metal Finishing Industry, and uses in industries having similar pollution problems.

Cell Design

The cells used in this demonstration are described in detail in Section VI. These cells use electrodes as baffles, creating an upward and downward directed flow through the bed. Each bay (or compartment) represents 20 percent of the total bed length.

At low levels of contamination (below 5 mg/l), the required contact time within the bed becomes much lower. Cells have been employed which have the same general anode to cathode spacing and bed width as in the demonstration units, with the exception that the bed length is shortened to the point that only upflow is used. These shortened cells have proved effective in reclamation of precious metals where economics dictate low level contamination. Lower capital cost per unit volume of hydraulic loading is realized by this alteration in cell design.

A logical extension of the single upflow cell just described is the circular cell. These cells use concentric electrodes with one of the major electrodes being the outer shell (or an electrode in close contact with a conforming shell) and the other electrode being centered within this shell. The semiconductive bed is placed between the electrodes and the flow of liquid is parallel to the electrodes.

A thorough description of this cell configuration is provided by Franco and Balouskus.[33] Their major effort was directed towards iron reduction under an EPA demonstration grant. The data presented shows the influence of the area relationships of the major electrodes. When reduction is the desired reaction, the outer electrode is preferred to be the cathode. It is believed that when the polarity is reversed so that the center electrode (with its smaller surface area) becomes the cathode and the outer electrode (with its larger surface area) becomes the anode, then the cell will exhibit improved oxidation properties. Cells using this basic concept have been evaluated on hexavalent chromium bearing waste water and have received limited market acceptance.

The cells demonstrated use a bed that is totally comprised of particles that are conductive and which exhibit the bipolar effect described earlier. Lancy[34] presents a modified cell in which there is intentional intent to separate the conductive particles with inert, non-conductive particles. It is believed that this alteration in cell design produces a greater potential between the conductive particles. Evidence to date from pilot plant applications indicates that the more refractory cyanide complexes (iron and nickel) are oxidized in this modified cell.

Metal Finishing Applications

The demonstration project addressed primarily the complete reduction of hexavalent chromium and the partial oxidation of cyanides coming from zinc plating. The amount of cyanide from copper and cadmium plating played a very minor role (less than 5 percent each). Other production experiences within the Metal Finishing Industry where this technology has been employed are worthy of comment.

In one job shop, cells comparable to those demonstrated are employed prior to a complete hexavalent chromium chemical reduction waste treatment installation to reduce the amount of chemical consumed in the chemical plant. Reduction in chemicals consumed in the range of 50-90 percent have been realized. In another job shop where the primary cyanide bearing waste is from copper plating, greater cell efficiencies have been realized. In this particular application, the normal cyanide level is less than one-fourth that experienced in this present demonstration. With the same contact time in the bed, all cyanide is oxidized and the copper content in the effluent is less than 0.5 mg/l. At a mid-western manufacturer of builders hardware, a cell similar to that demonstrated in this project is employed on rinse water following brass plating. In this case, the contamination level is in the same range as at New England Plating Company. Cell efficiencies greater than 99 percent have been continuously demonstrated. In these two applications, the applied voltage is in the range of 12-14 volts as opposed to the 40 volts required for the demonstrated waste stream with zinc cyanide. It should be noted that at this latter facility only cyanides measured by the silver nitrate titration technique are monitored. The results of treatment relative to the iron cyanide complex known to exist in this waste water cannot be reported.

Rectangular cells similar to those employed at New England Plating and single upflow cells described earlier have been used in production applications for gold reclamation. In the case of the longer cell contact time, the gold is completely retained within the cell and the cyanide (less than 3 mg/l) is oxidized. In the cases employing the lower contact time, attention is directed solely to gold reclamation. In these applications, the values attributed to the gold reclaimed from the bed provides an entirely different economic incentive than when only waste treatment is considered.

In the application of conversion coatings to aluminum, a common additive to the hexavalent chromium containing process solution is sodium ferrocyanide. This additive enhances the gold color desired by consumers. A production installation using a cell as demonstrated is used for simultaneous reduction of hexavalent chromium and removal of the ferrocyanide. Contamination levels are comparable to those at New England Plating for hexavalent chromium and approximately 3-5 mg/l for the cyanide.

The modified cell described by Lancy[14] has received extensive evaluation in pilot plant sized equipment. In one application, a solution of sodium chloride is recirculated in a manner similar to the well-known Lancy Integrated System. As the chloride solution passes through the modified cell, sodium hypochlorite is produced. As cyanide is introduced into this closed loop system (simulating dragout on work pieces), the cyanide is oxidized with the hypochlorite to produce cyanate and chloride. The chloride is again available for re-oxidation to hypochlorite. It is expected that operating economies will be realized and that lower chloride contamination will be available when this application is fully developed.

In the other application of this modified cell, attention is being directed towards oxidation of cyanide complexes experienced in the immersion stripping of nickel from steel. Pilot plant efforts indicate that this low temperature process effectively oxidizes this more refractory complex. It is expected that production experience in this use will be obtained in Europe during 1974.

Applications Outside of Metal Finishing

Several applications of the same basic semi-conductive bed technology have met with positive results in fields outside of metal finishing that are similar to problems within this industry.

In a copper rolling mill, rinse water following sulfuric acid pickling contains approximately 35 mg/1 dissolved copper at a pH of 2. As this waste passes through the bed, copper is deposited at cathode sites. The cell discharge is virtually copper free (less than 0.5 mg/1). Subsequent pH adjustment to neutralize the acid is provided. Due to the low copper content in the cell discharge, no copper hydroxide is produced. The need for solids separation and sludge disposal is eliminated by extracting the copper as copper metal.

Ferrous iron common to acid mine drainage has been oxidized to ferric iron in round cells. The sludge stability problem attendant with ferrous hydroxide is eliminated. These are indications that a more dense sludge is formed by the electrolytic process than that obtained by air oxidation. Details of this particular demonstration project are provided by Franco and Balouskus.[33]

Rectangular cells are being used to collect trace quantities of platinum group metals in a refinery. The waste water is low in pH (about 0.5). The value of the metals collected on the carbon bed provides economic incentives for using the technology. Considerations are being given to using the process in place of the cementation process currently being used prior to the electrochemical process.

The same modified cell described earlier in work being done on nickel cyanide strip is being used for oxidizing cyanide heat treating salts. In this application in West Germany, the primary concern is for removal of ferrocyanides.

GUIDANCE FOR OTHERS

Should others faced with resolution of pollution problems wish to consider application of the technologies being reported for this demonstration project, it is suggested they consider the following comments.

Water Conservation

The use of counterflow rinses provides significant reduction in water use. The extended counterflow expands upon this concept. In using the extended counterflow technique in cleaning cycles, one must consider the type of cleaner in use. Heavily silicated cleaners may produce a precipitate on the surface of the work pieces when the cleaner film is acidified. This silicate film may require the addition of fluoride salts to the pickle so that they will redissolve in the pickle.

Good mixing is required. Introduce the incoming water at the bottom of the rinse tank and overflow the top. Existing facilities may not have sufficient hydraulic head between rinse tanks which were not designed for counterflow rinsing to permit the use of small diameter piping. At New England Plating, 7.6 cm (3 in.) diameter pipe permitted the desired flows to be obtained.

Virtually all of the evaluations of this extended counterflow rinsing approach to the plating solution itself has been done on zinc and cadmium plating. With these two process solutions, immersion deposition of metals is not experienced. Caution must be taken when other metals are being processed, and a thorough evaluation is recommended by others looking for the advantages of extended counterflow rinsing.

In the re-use of treated water (with or without suspended solids removal) one must consider subsequent processing. With further cleaning operations, as in this demonstration project, preliminary cleanliness is not essential. Obviously, treated water may be used for maintenance cleaning. It should not be considered for applications where solids (dissolved or suspended) present problems as in the addition to plating tanks and final hot water rinses.

In all efforts directed towards water conservation, a prerequisite is a thorough knowledge of the various metal finishing operations employed.

Electrochemical Reduction of Chromium

In considering the application of electrolytic reduction of hexavalent chromium, the maximum contamination level must be established prior to selection of equipment size to produce the desired discharge level.

Purveyors of equipment for this application will be able to answer questions as to the tolerance level of their cells. It is believed because of the interest established in this technology that many of the relatively high costs associated with capital and operating expense will be resolved.

Where the process is used in cost reduction efforts prior to a chemical treatment system, it is obvious that less demands will be placed upon the cell design.

Control of raw waste pH is essential to the successful application of this process. The maximum pH selected will depend upon the equipment itself, the concentration of hexavalent chromium and the degree of removal required.

Electrochemical Oxidation of Cyanide

Greater caution is required in the application of the electrolytic process to cyanide bearing waste. The role of metals normally associated with cyanide complexes in the metal finishing industry is not fully understood when electrolysis is employed.

In using this technology one must consider the hardness of rinse water. Production experience has shown that when the rinse water is "hard," calcium carbonate is produced within the cell and precipitates from solution due to its low solubility. In hard water areas, water softening is an essential prerequisite.

Oil should be kept from entering system to prolong carbon life.

As with using the process in reduction applications, the equipment suppliers should be consulted in each application to avoid misapplication. Today's negative features may well have been overcome for many uses.

Suspended Solids Removal

The advantages of the "tube" settler in reducing capital costs and space requirements have been demonstrated on treated plating waste water. Several purveyors of this type of equipment exist, each having their own unique features.

Sludge recycling appears to show a significant improvement in the clarity of effluent.

Sludge Concentration

A centrifuge provides a small compact tool for the production of thickened sludge. It is believed that less labor is required than with filtrations.

Multiple passes can be employed to reach the desired solids concentration.

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